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Selected Methods for Detecting and Tracing Hazardous Materials Spills

Calspan Corp, Buffalo, NY

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March 1979

SELECTED METHODS FOR DETECTING AND TRACING HAZARDOUS MATERIALS SPILLS

by

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Contract No. 68-01-0110 and 68-03-0287

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CINCINNATI, OHIO 45268

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes studies conducted to evaluate the use of several selected off-the-shelf techniques to detect and monitor spills of hazardous materials in the water environment. Techniques studied included pH, conductivity, colorimetry, ion specific electrodes, catalytic combustion sensors, and dye tracing. Based on these techniques both a prototype device to give early warning of spills of heavy metal compounds and a field detection kit to trace the location of several hazardous materials were built and tested. This report should be of value to Federal, state and local government personnel as well as to individuals from the chemical process and transportation industries who are involved in responding to discharges of hazardous substances. Information on this subject beyond that supplied in the report may be obtained from the Oil and Hazardous Materials Spills Branch (IERL), Edison, New Jersey 08817.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Detection of hazardous chemicals by a wide range of phenomena including electrical conductivity, catalytic combustion, and colorimetry was investigated. This study showed that simple, fieldable instruments are available or can readily be made available for detecting spills of most common, hazardous materials at or near the threshold for deleterious biological effects. Several applicable commercial instruments were identified. A novel apparatus employing chemical indicators was developed for the early warning of spills of a wide range of pollutants in natural water bodies. A prototype spill tracing kit was designed and fabricated for use by laymen and its effectiveness demonstrated with volunteer firemen as operators.

This report was submitted in fulfillment of Contract Nos. 68-01-0110 and 68-03-0287 by Calspan Corp. under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period June 30, 1971 to February 25, 1974, and work was completed as of March 20, 1974.

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SECTION 1

INTRODUCTION

For the effective treatment of spills of hazardous materials, it is imperative that the spill be detected and identified rapidly and that the geographical extent and concentration of the spilled material be monitored during the course of the treatment. Rapid detection of the spill facilitates treatment, which is almost always more effective with the concentrated spills, and permits reduction in the contact between biotae (including humans) and the hazardous substance by localized treatment, impoundment, closing of municipal water intakes, etc. Delineation of the amount and extent of untreated material permits cost-effective treatment and limits the exposure of the environment to excess treatment chemicals.

At the present time early notification of a spill depends on the report of the person responsible or on environmental signs which are obvious to untrained observers (gross changes in color, odor, fish behavior, etc.). On the other hand, in certain high-probability locations, such as harbors and industrial rivers, arrays of automatic spill detection/alarm systems could be effective. To maximize the ratio of spill damage prevented to instrumentation cost, such systems should be broad based, i.e., react to a wide spectrum of possible pollutants. Furthermore, to be suitable for such applications, instrumentation must require little maintenance and be resistant to deterioration in the hostile environment characteristic of sewers and industrial rivers.

The requirements for equipment and methods of monitoring the extent of a spill and the progress in its treatment are somewhat different. Such equipment does not require the same degree of environmental immunity as the spill alarm probes since it need be deployed only during the treatment of a spill and need survive only a few hours of environmental exposure. Temporary deployment also obviates the need for extended periods of maintenance-free operation and permits rather rapid expenditure of consumables, e.g., indicator chemicals. Since an operator can be deployed with the equipment, automatic operation is not necessary and a rather complex signal processing computer (the operator) is available for interpreting the equipment outputs. Finally, a few highly portable instruments can cover a rather wide area of possible pollution sites by being deployed to a previously reported spill site. On the other hand, this field-monitoring equipment must give semiquantitative results -- such as an indication of the endpoint of the spill-treatment titration, and should provide a fairly specific indication of the nature of the spilled material. Furthermore, although an operator is available, he may not be skilled in chemistry or electronics. The instrument therefore should require only the observational skills of the average person, such as

viewing a color change from a colorimetric indicator, or reading a pre-calibrated meter.

During 1971-72, Calspan Corporation, under contract to the Environmental Protection Agency (EPA), undertook a study to select methods and instrumentation that are commercially available or could be quickly developed to meet the aforementioned spill alarm and/or field monitoring criteria, with major emphasis on applications to the detection and monitoring of spills in watercourses. A wide range of chemical and physical phenomena were explored in this effort, and are detailed in the body of this report. Among the devices evaluated were: conductivity meters for ionic solute spills; pH probes for acid or base spills; specific ion probes; catalytic combustion sensors for volatile organics; and a multicolor transmissometer for non-volatile organics. In addition an automatic "cyclic colorimeter", which uses modulation of indicator injection to compensate for turbidity and fouling, was developed under Contract 68-03-0110 and field tested under Contract 68-03-0287. Other experiments indicated the effectiveness of dyes as spill tracers and of the sense of smell as a spill detector. Perhaps the most significant outcome of the effort was the development of a spill detection kit containing a conductivity meter, pH indicator, odor samples, and colorimetric reagents geared to the prescribed spill treatments. This kit has been proven effective in tests involving volunteer firemen as operators.

SECTION 2

CONCLUSIONS

Electrical conductivity was found to be highly effective in detecting the presence and measuring the extent of untreated ionic solute spills but was essentially worthless in indicating the effectiveness of the treatment.

Commercial pH probes and certain other specific ion probes proved to be highly effective in detecting and measuring spills of acids, bases, and metallic salts and in monitoring the effectiveness of their treatment.

Volatile organics triggered indications from commercial catalytic combustion sensors while less volatile organics were detected with a multicolor transmissometer.

Colorimetric indicators proved to be extremely helpful and were used both in a spill detection kit designed for use by volunteer firemen and in an automatic "cyclic colorimeter", which uses modulation of indicator injection to reduce its sensitivity to turbidity and fouling.

Colorimetric indicators were not reliable when added to a water body (e.g., as a stripe sprayed from a low flying airplane) to delineate the extent of an acid or base spill.

Experiments indicated the effectiveness of dyes as spill tracers and of the sense of smell as a spill detector.

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The cyclic colorimeter is a useful instrument for field monitoring of spills. An evaluation of its characteristics showed that it maintained adequate sensitivity of a few parts per million of heavy metal ion for a period of about two weeks without maintenance and despite noticeable fouling due to scale buildup and stream turbidity. However, it proved difficult to make a simulated spill that would not be suppressed by natural processes in the creek without spilling unconscionable quantities (tens of moles) of simulant.

SECTION 3

RECOMMENDATIONS

A kit of instruments and reagents should be developed to detect and define the location of previously identified spills. The kit should be made available to appropriate federal, state, local agencies that may be required to respond to spills of hazardous materials. A short educational movie on the proper use of the kit should also be produced and made available to these agencies.

The fact that pH electrodes have been provided with considerable resistance to fouling and other interferences suggests that the same could be done for other specific ion electrodes, e.g., sulfide, bivalent metal, and cyanide probes. Some research and development in this area is in progress. This effort should be encouraged.

Instruments to be incorporated in a device for treating spills of hazardous substances were developed to a point where they could be tested in a controlled environment. Such tests should be conducted to establish stability and accuracy of this treatment approach.

A multidetector hazardous spill warning system should be developed to detect spills of broad classes of compounds.

SECTION 4

EARLY WARNING TECHNIQUES

CONDUCTIVITY MEASUREMENTS

Conductivity is traditionally used as a measure of purity for distilled and deionized water. Since the conductivity of fresh water in most streams and lakes is fairly low (50 to 500 S/cm*)(1), a sudden increase in conductivity indicates the presence of an ionic solute, probably a pollutant. Conductivity is usually measured with alternating current to avoid interference from a plethora of ionic reactions which occur when direct current is applied to electrodes in water. In the laboratory one uses platinum electrodes whose geometry is calibrated against solutions of known concentration in a sample container, an AC source operating at a few hundred hertz, and electronics of varying complexity, depending on the amount of automation one can afford. For field use, a rugged conductivity meter that uses very little power and is capable of being read at some distance from the electrodes that are to be dipped into a stream is desired.

One such instrument (shown in Figure 1) was developed for use in sewers, where it discriminates between sewage and oil accumulations in traps. (2) It is extremely rugged, as attested by its continuous use for several years in an inverted syphon in Buffalo, New York. Conductivity is measured by the load presented to a small radio frequency oscillator immersed in the fluid. (3) Regrettably, it is most sensitive to variations of conductivity in a range typical for oil pollutants and very pure water. An attempt during this study to extend its range to the less pure water in natural waters failed.

Figure 2 presents data on the impedance of one centimeter cubes of various salt concentrations as a function of frequency. The more rapid variation in impedance with concentration at lower frequencies indicates that low frequency measurements should be used if pertinent levels of pollutants are to be discriminated. Although several commercial instruments can measure audio-frequency conductivity, none is suitable for spill monitoring. To fill this gap, a simple, inexpensive, telemetering device was developed. The instrument (Figure 3) consisted of a unijunction transistor (Q_1) used as an oscillator, a pulse amplifier (Q_2), the dual of a Wien bridge used as a filter ($R_1C_1R_2C_2$), a silver electrode (UG-1094 connector) which sensed resistance in the path between it and the instrument case (a one pint tin can), a rectifier ($C_3C_4D_1D_2$), and a transistor (Q_3) which controlled the frequency of oscillation of the UJT(Q_1). This frequency, ranging from 200

*The Siemen (S) equals and replaces the mho unit of conductance.

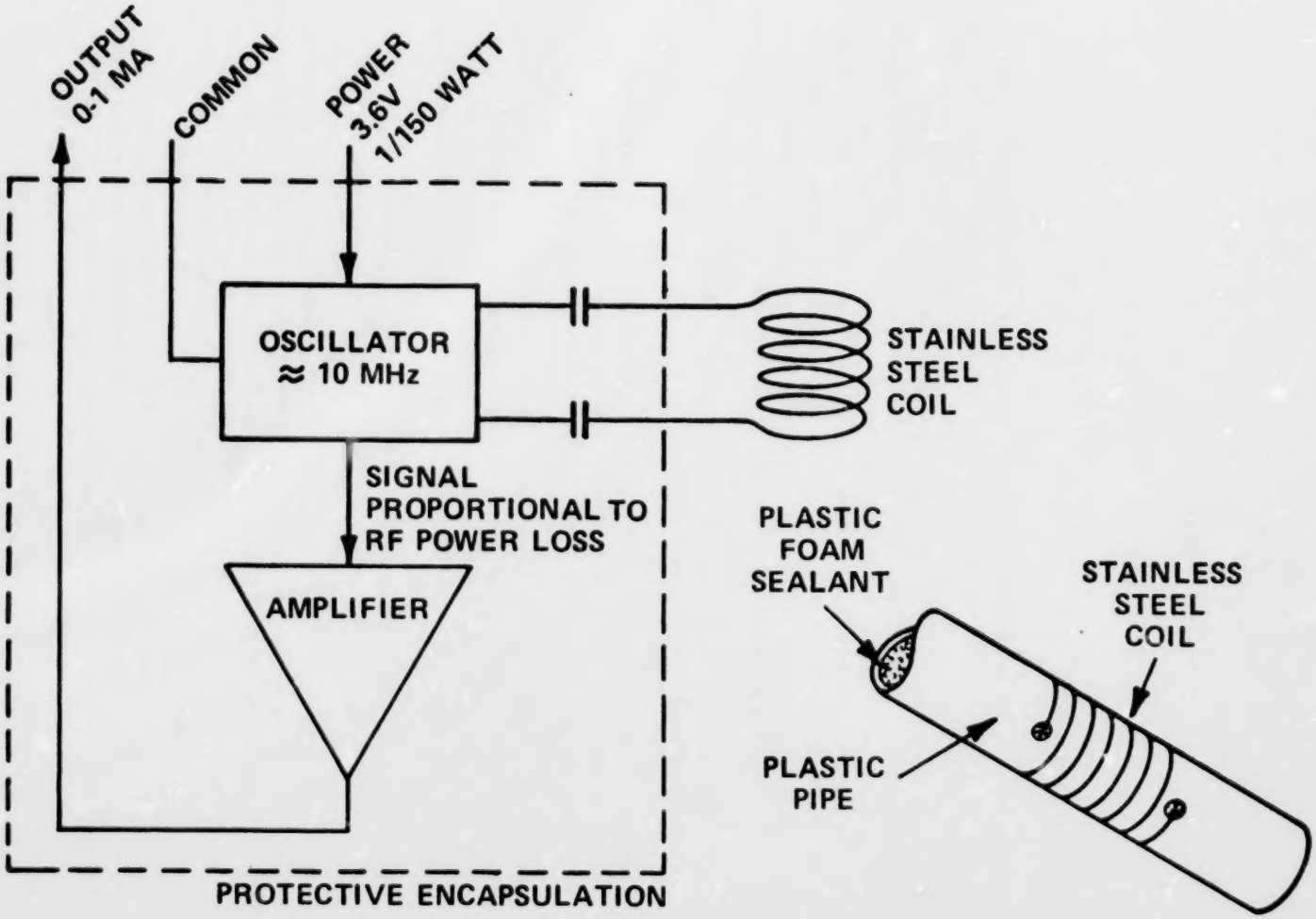


Figure 1 RADIO-FREQUENCY OIL SENSOR

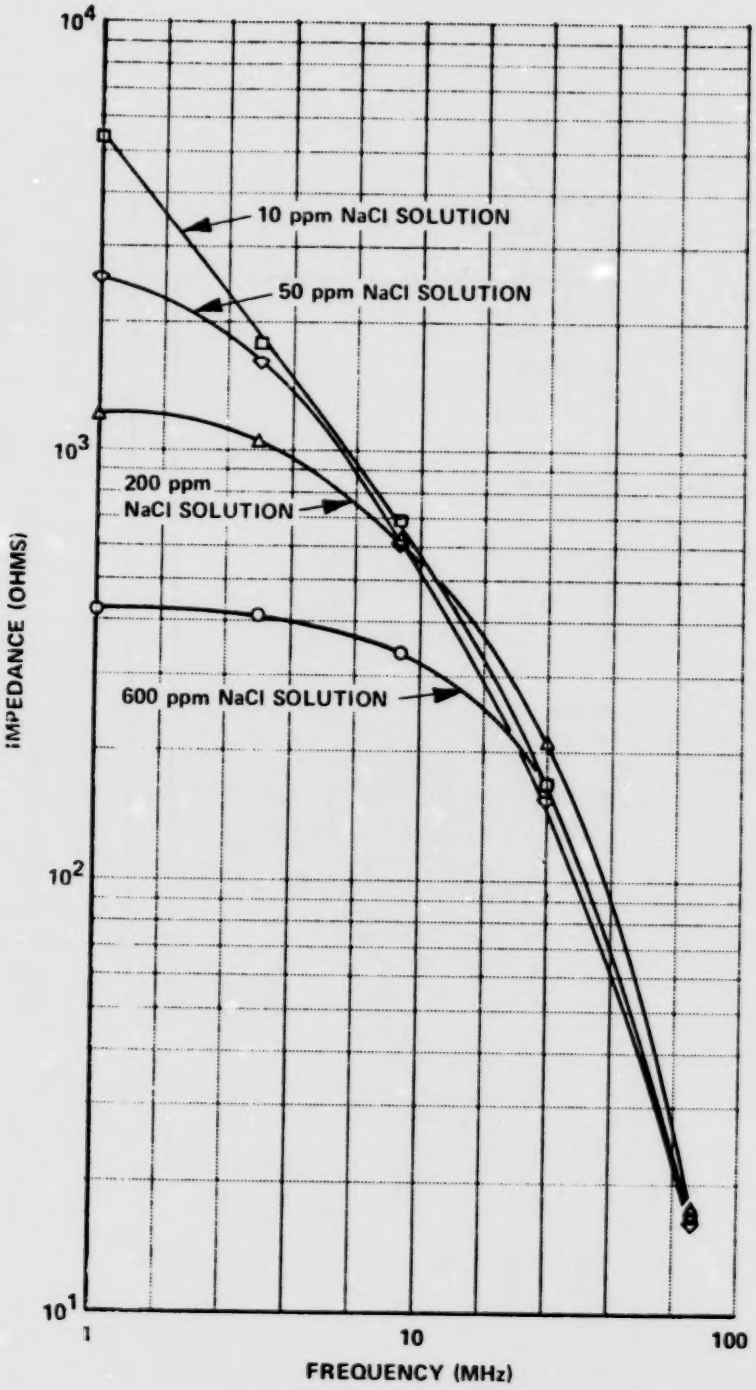


Figure 2 SOLUTION IMPEDANCE VS FREQUENCY

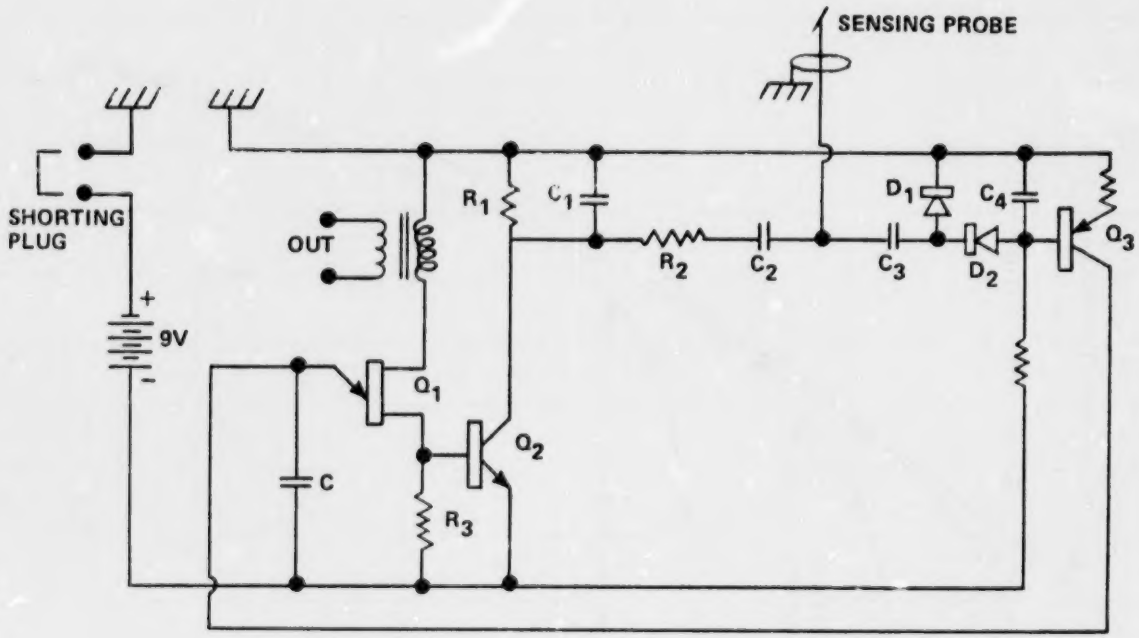


Figure 3 EARLY CONDUCTANCE METER

to 3000 hertz as a function of resistance, was carried to shore on a two-wire, transformer-coupled line.

Figure 4 shows a record obtained with this conductivity meter during a full-scale simulation of a heavy metal spill. Five moles of ferrous sulfate solution (about 280 grams of the salt) had been added to a creek five meters upstream of the conductivity meter. At the time of the simulation, the slug was about 25 meters long, 2 meters wide, and 0.2 meters deep. It was estimated that the concentration of Fe^{++}, averaged 28 ppm, ranging between 30 and 100 ppm. Flutter and wow in the small, battery-operated tape recorder used to obtain this record contributed the broad ribbon of noise, and its tape skip caused the spikes seen in the figure.

After this test, an improved tape recorder was obtained and the circuit of the conductivity probe was redesigned. The functions of the pulse amplifier (Q_2) and frequency modulator (Q_3) transistors were replaced by passive elements and the conductivity probe appeared as shown in Figure 5. The transistor (Q) operates as a blocking oscillator with a transformer (T) which also couples output signal to the shore cable. Frequency is determined by the voltage across the base resistor R_3. This voltage is obtained partially from a prebias resistor R_4 and partially from a rectifier, probe, and Wien bridge dual as in the earlier unit. Total power consumption is only a few milliwatts from the single 3-V battery. The cost of this unit is negligible compared to that of the recorder or meter readout ($20) and a waterproof case with stainless steel electrodes ($10).

A third version of the contacting conductivity probe (Figure 6), using integrated circuits, was also constructed. Although this circuit is more complex, containing four active gates rather than one transistor, most parts have been joined in the integrated circuit, and assembly is very simple. Power consumption is even lower than for the earlier circuits and a direct meter readout is practical. This circuit is useful for taking manual readings, typically in tracing an existing spill, while the circuit of Figure 5 is more suitable for recording and telemetry applications, such as for detecting the approach of a spill at a preexisting sensor. For this reason, it is the circuit of Figure 6 that has been used in the spill tracking kit described later in this report.

The efficacy of conductivity as an indicator of pollutants, unfortunately, is not matched by its performance as an indicator of treatment efficiency. For example, laboratory measurements of conductivity during the titration of mercuric chloride with sodium sulfide showed no readily detectable changes in slope or magnitude either at the correct stoichiometric ratio for complete precipitation of the mercury as sulfide or at the point where the mercury redissolves in excess sulfide ion concentration. The measurements did show, however, that redissolution of the mercury requires a tenfold excess of sulfide ion concentration over that required for correct stoichiometric treatment, a rather favorable margin for treatment error.

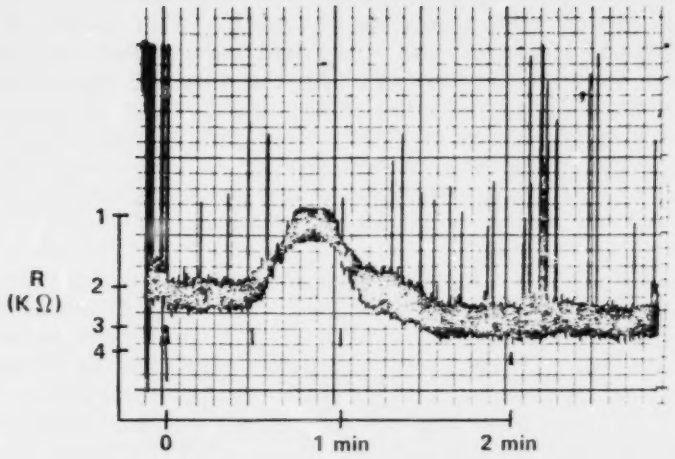


Figure 4 CONDUCTIVITY METER RECORD – SIMULATED SPILL

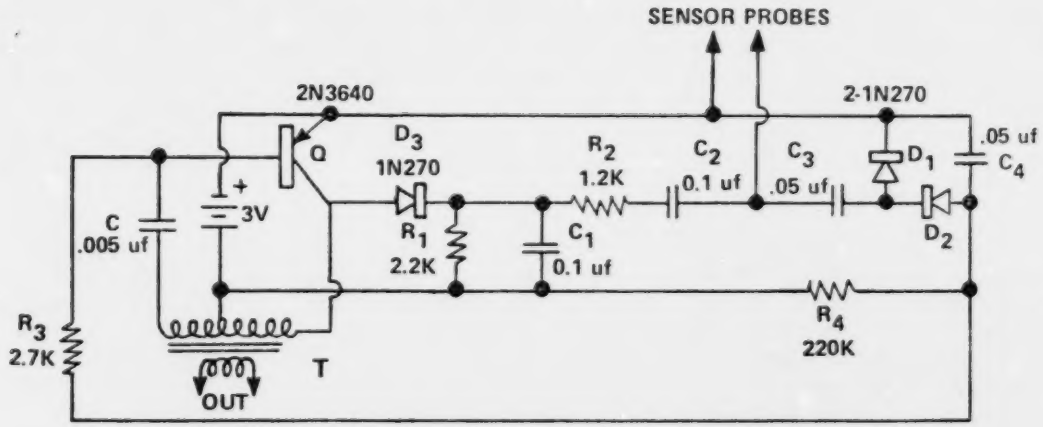


Figure 5 SIMPLIFIED CONDUCTANCE METER

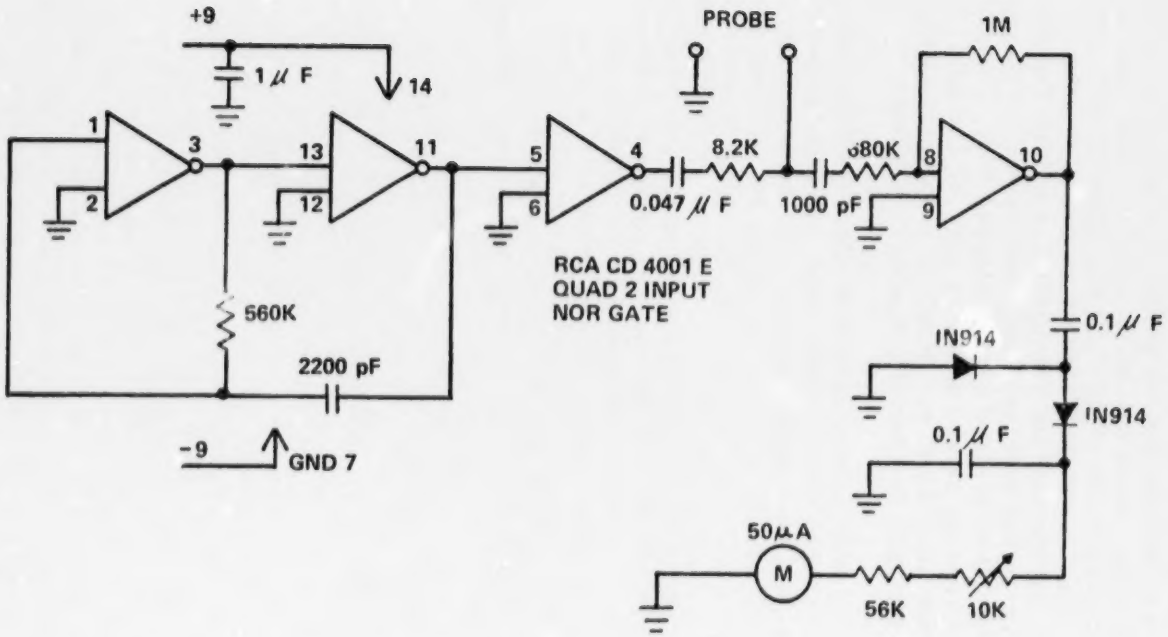


Figure 6 HASP CONDUCTANCE METER MOD "C"

SPECIFIC ION ELECTRODES

Electrodes for pH measurement have advanced from the laboratory to on-line control capability and have found wide application in pollution monitoring. They have been used in oceanography, where compensation for high ambient pressure is necessary (4), and nonfouling probes are commercially available. (5) Specific ion electrodes, which are quite similar, were used in this program to trace the concentration of sulfide and bivalent metal ions in spill simulations. Figure 7 shows profiles of sulfide ion taken at four stations along a stream during sulfide precipitation of the ferrous sulfate spill referred to earlier. The readings were made visually from commercial specific ion meters, and later plotted versus elapsed time. All four curves were made with two instruments; as the trailing edge of the spill passed the upstream instrument, that instrument was moved to a position downstream from both the second instrument and the leading edge of the plume.

Data from laboratory simulations indicated that specific ion probes are quite sensitive to turbulence in the stream flow. Commercially-available electronics for such probes have fixed internal time constants so short on some instruments that turbulence noise is excessive and so long on others that meaningful measurements cannot be made in fast flow situations. In addition, the commercial instruments are not designed to facilitate or even permit the use of multiple probes in a single solution. To avoid these difficulties, new electronics (Figure 8) were designed and constructed with selectable time constants and truly differential input and output. These electronics were tested against commercial electronics in a 10 cm wide flow channel. With a time constant of 0.1 second, the new electronics outperformed the various commercial systems in ability to reject common mode and turbulence noise while responding much more rapidly to real changes in pollutant level.

CATALYTIC COMBUSTION SENSORS

Several commercial catalytic combustion sensors or vapor "sniffers" were evaluated as possible detectors of various chemicals chosen to represent broad classes of pollutants. In one series of experiments, a Johnson-Williams Model CD 830 was used in the configuration shown in Figure 9 to sense the vapor of the target chemicals in equilibrium with aqueous solutions of known concentrations. The sensor, an electrically-heated platinum wire whose temperature is further raised by the catalytically-induced oxidation of any combustibles in the sensed atmosphere, was mounted in a beaker. The beaker was inverted over a second beaker containing distilled water to which the pollutant was added in steps. Except for an adjustment of the gain control to its maximum value, the electronics of the detector were not modified from the "as received" condition. Under these conditions, the output voltage of the detector exhibited a drift of 0.7 mV per eight-hour day and a temperature coefficient of 0.1 mV/^{o}K. With these uncertainties, a reasonable estimate of the detection limit is that concentration which produces a 1 mV output signal. Since the detector response is linear with aqueous concentration of the target, the detection limit figure is also the sensitivity in ppm/mV.

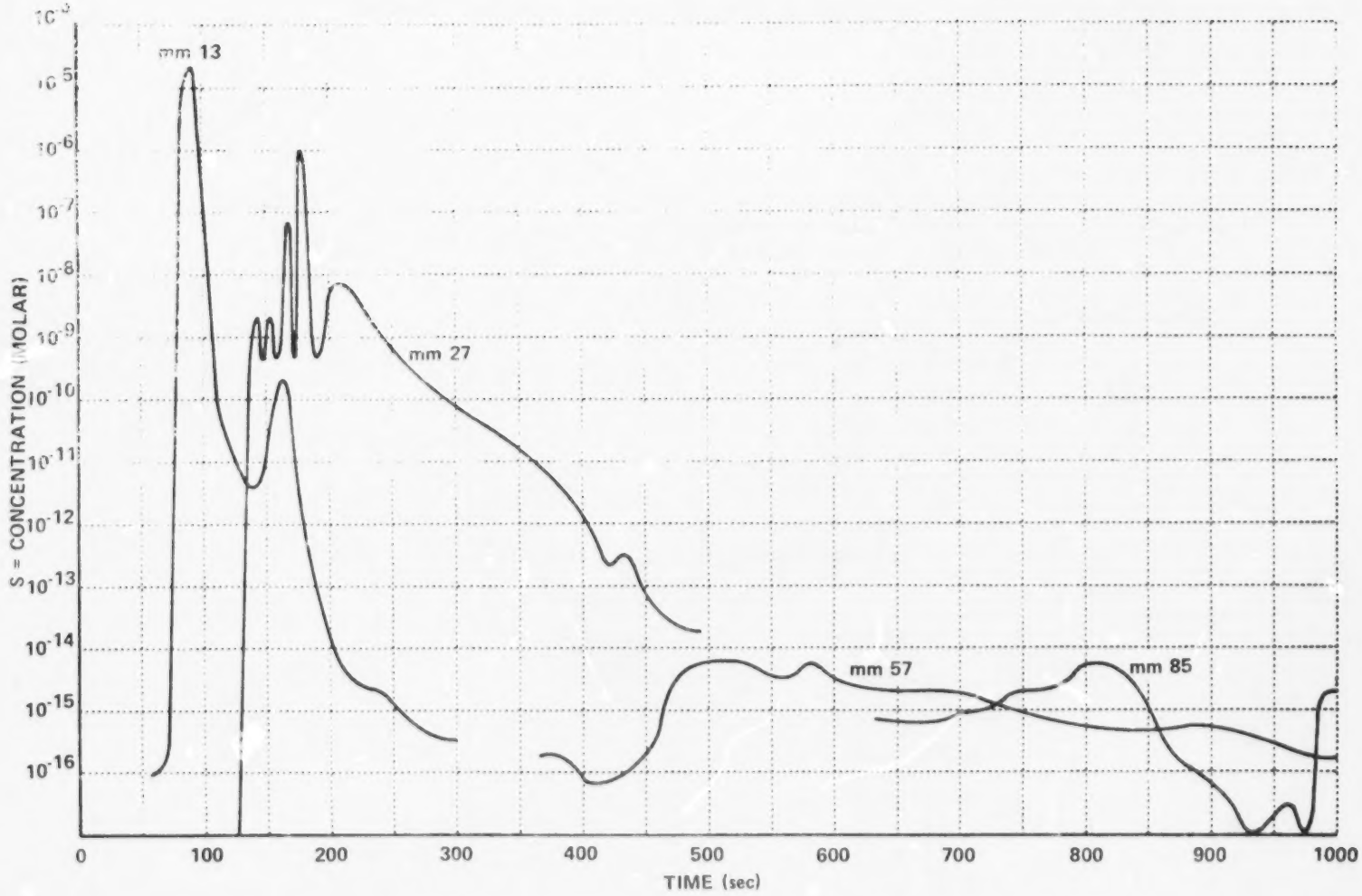
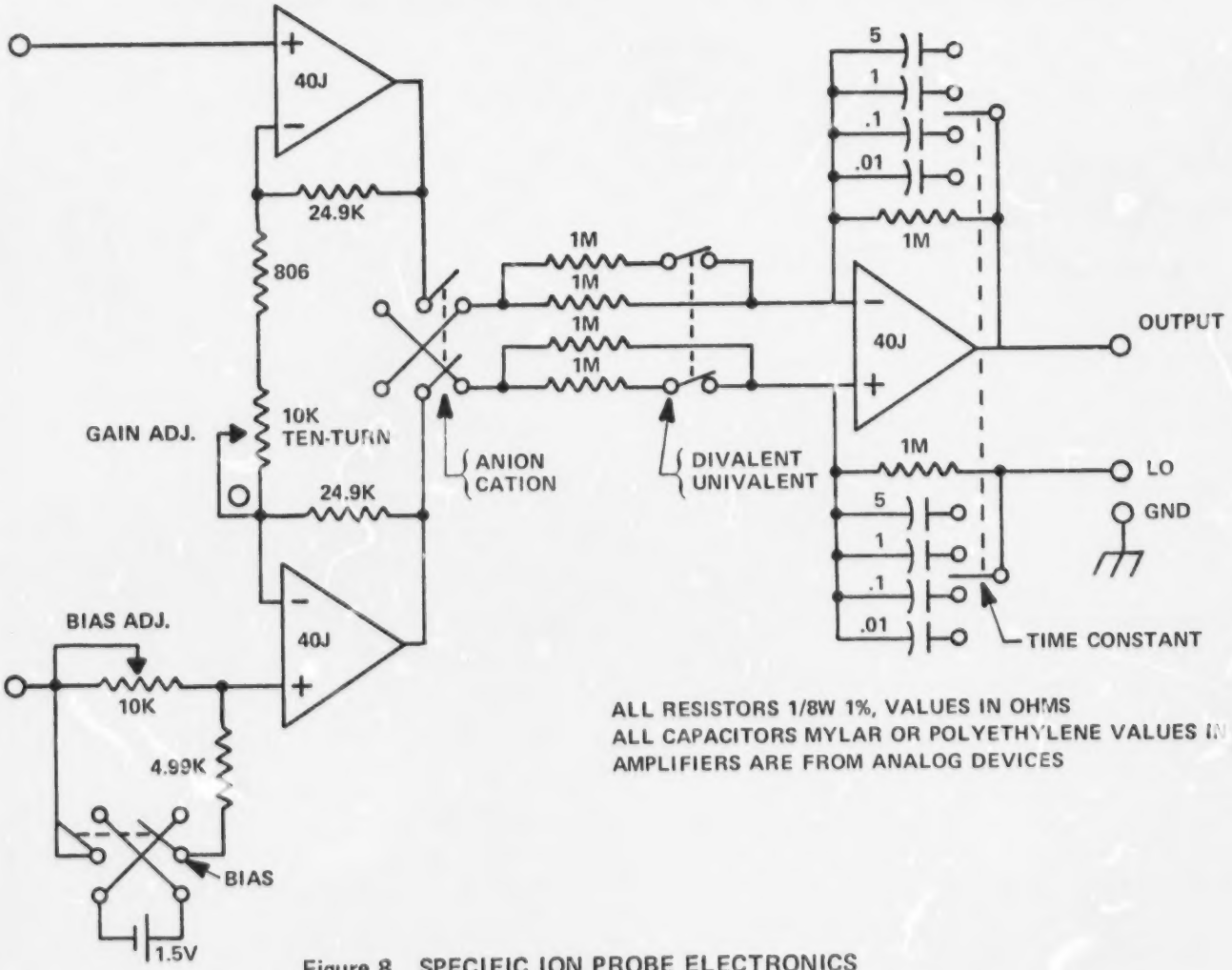


Figure 7 SULFIDE ION CONCENTRATION VS TIME AT SEVERAL SAMPLING POINTS



ALL RESISTORS 1/8W 1%, VALUES IN OHMS
ALL CAPACITORS MYLAR OR POLYETHYLENE VALUES IN μF
AMPLIFIERS ARE FROM ANALOG DEVICES

Figure 8 SPECIFIC ION PROBE ELECTRONICS

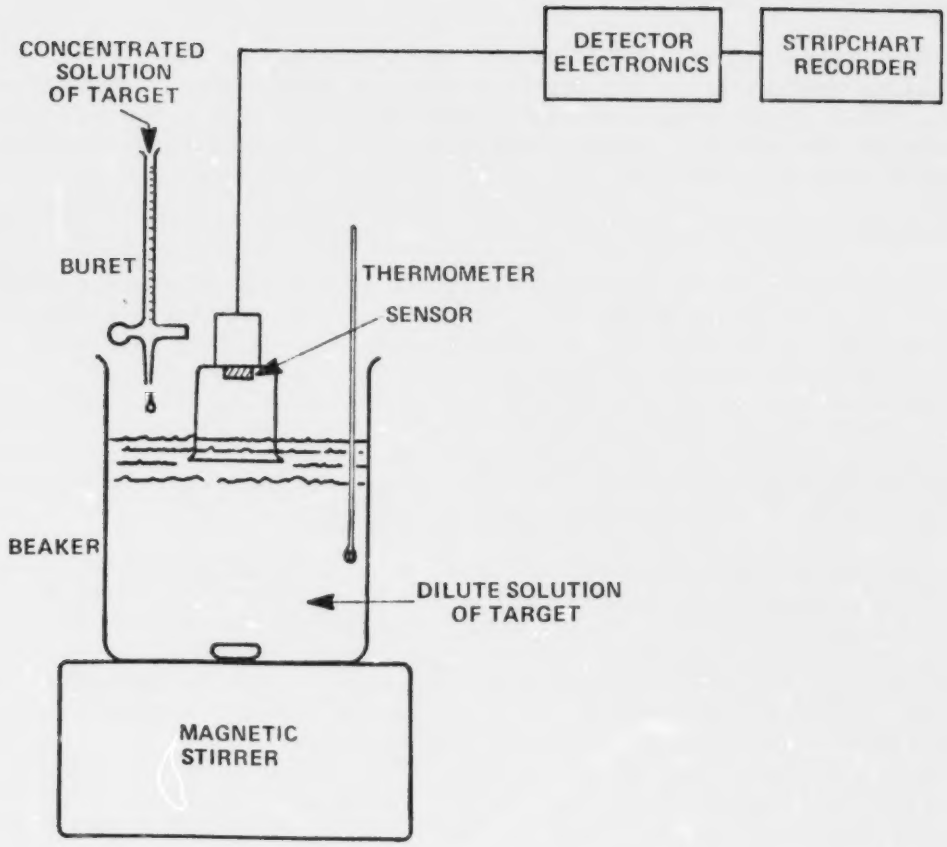


Figure 9 "SNIFFER" EVALUATION APPARATUS

Table 1 presents the observed detection limits for several representative chemicals and compares them with the respective critical concentrations, i.e., levels at which behavioral effects are noted in fish. Note that the detection limit is within a factor of three of the critical concentration for methyl alcohol and acrylonitrile, so the combustible vapor detector should serve as a good spill detector for these two chemicals. The factor of 62 for ammonium hydroxide might be tolerable, but the response is orders of magnitude too low for the detection of chlorine, phenol, and acetone cyanohydrin in solution.

Also listed in the table are the time constants of the system, both for increasing concentration and for flushing with fresh water. These data show that a spill at the detection limit would be "seen" within two minutes of its arrival at the sensor. Spills involving higher concentrations would be detected much more rapidly.

MULTICOLOR TRANSMISSOMETER

A substance can be defined or assigned to a group of similar substances on the basis of measurements of its transmissivity at several discrete wavelengths. To accomplish this discrimination, weighting factors are applied to the transmissivity measurements which are than summed. For the transmission spectra of the substances and filters involved, matrix analysis can derive sets of weighting factors which effect optimal separations among the various substances. Discrimination can be improved by using n sets of weighting factors to separate the substances in n-space and computerizing the processing of the transmissometer output.

The effectiveness of such an approach is shown in Figure 10, where two sets of weighting functions applied to measurements at five different wavelengths are used to discriminate among seven substances (water, JP-1, brake fluid, ethylene glycol, Shell aviation 115, aviation hydraulic oil, and 10W-30 motor oil) for which transmission spectra were readily available. Each "cloud" is formed of one point each for the pure target substance, the target contaminated 10% with each other substance, and the substance contaminated 20% with each other pair of substances. The present computer program develops five weighting functions, but, as can be seen from Figure 10, two are sufficient to separate these substances even in the presence of the 20% contamination.

The optical transmission spectra of the chemicals in Table 1 were examined to determine the feasibility of identifying these pollutants with the multispectral detector. Only the phenol spectrum exhibits sufficient structure to enable its identification by the multispectral technique. However, colorimetric indicators which produce recognizable spectra for ammonia and chlorine have been identified which are compatible with unattended detector operation.

In the case of ammonia, two drops of ammonia stabilizer and one milliliter of Nessler reagent were added to 50 milliliters of a 290 ppm solution of ammonium hydroxide. The test solution immediately turned orange and slightly cloudy. The spectral transmittance curve of this solution is

Table 1

"SNIFFER" RESPONSE TO GROUP A CHEMICALS

Chemical	Critical* Concentration (ppm)	Detection Limit (ppm)	Detection Limit / Critical Concentration	Response Time (sec)	Flushing Time (sec)
Ammonium Hydroxide	5.0	310	62	90	60
Chlorine	0.03	-3300**	10^5		
Methyl alcohol	250	700	2.8	120	90
Phenol	0.1	8000	10^5	330	60
Acrylonitrile	15	45	3	60	15
Acetone Cyanohydrin	1-100	$2x10^4$	10^4	120	15

* Concentration at which behavioral effects are observable

** Response of opposite polarity (depression of combustion)

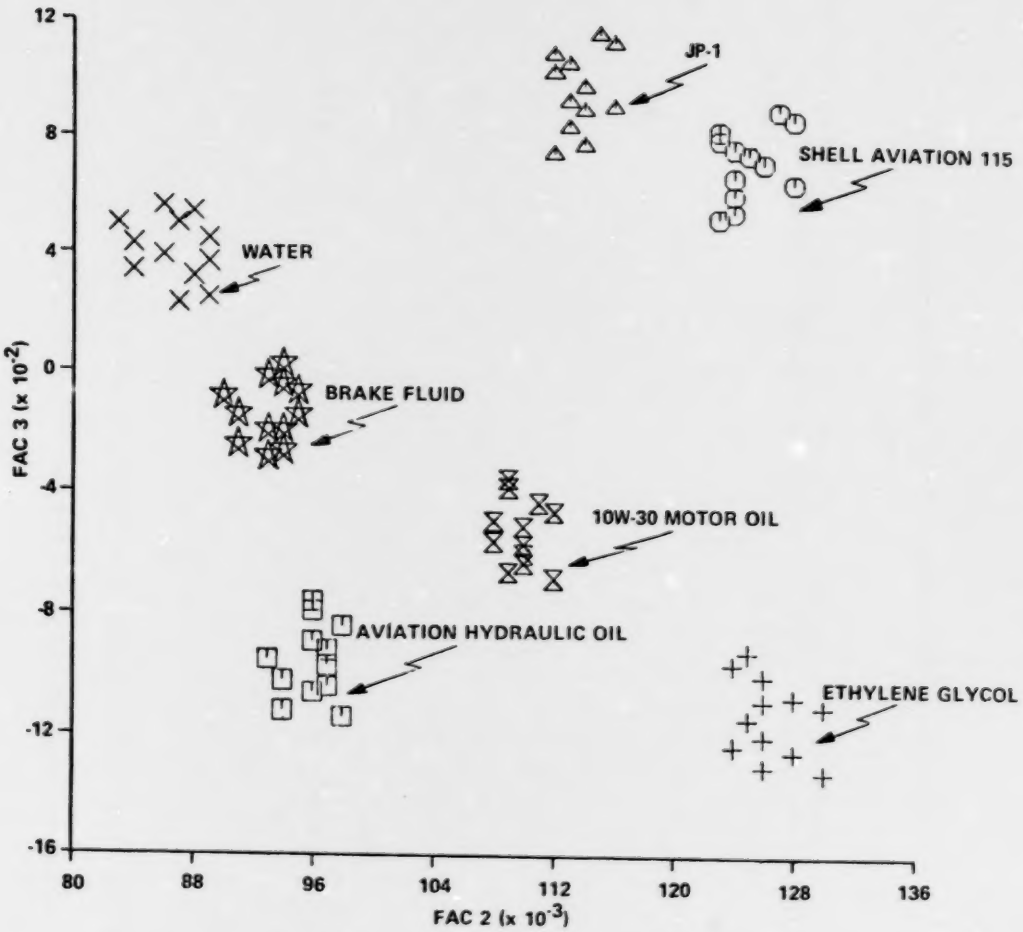


Figure 10 SPECTRAL DISCRIMINATION OF SEVERAL MATERIALS BY USE OF WEIGHTING FUNCTIONS

easily distinguished. For chlorine, two drops of orthotolidine reagent were added to 20 milliliters of sample solution having a chlorine concentration of 70 ppm. The solution turned orange-pink and its spectral transmittance curve indicated a clearly distinguishable minimum at approximately 380 nanometers.

For acetone cyanohydrin, a test was made using vanillin in an alkaline solution as a possible indicator. The reaction produced a brown color in the test solution, but the reaction proceeds slowly unless the temperature of the sample and the reagent is raised above room temperature. Also, when the reagent solution containing the vanillin and potassium hydroxide was added to distilled water as a control solution, the control solution itself was unstable and gradually changed color. Although the color reaction in the control solution was much slower than that observed for the 1000 ppm acetone cyanohydrin test solution, this particular colorimetric indicator was judged generally unsuitable for field use. Suitable indicators were not identified for acrylonitrile and methanol.

The complementarily of the "sniffer" and the multispectral detector is demonstrated by the above-mentioned data. The "sniffer" is a very good spill detector for methyl alcohol and acrylonitrile, two chemicals invisible to the multispectral detector, while it cannot detect phenol, which can be easily identified by the multispectral detector. To detect phenol and similar compounds, the development of an unattended multispectral detector was undertaken.

Some time ago, a two-color transmissometer, shown in Figure 11, was evaluated by Calspan for detecting oil in sewers. (3) It operated in the near-ultraviolet and red visible regions of the spectrum. The problems with implementing this approach in an unattended sensor are fairly obvious; one cannot expect precision optics to perform well for any duration under water. This was demonstrated when the two-color transmissometer was operated for about six weeks in a Buffalo sewer. Using the two colors, it was possible to detect when fouling had occurred. The oils that were to be detected were fairly opaque in the near ultraviolet and at least translucent for red light. If the red light signal that was periodically radio-telemetered to the laboratory at Calspan disappeared, it could be assumed that the device was fouled. During the second week of the test, scale from hard water fouled the apparatus. After cleaning the dilute hydrochloric acid it remained usable for over one month, when the UV emission from the argon lamp became too weak for further use. During this time, only one oil spill was detected. From the calibration of the instrument, a concentration of tens of parts per million was estimated; a sample taken shortly after detection contained hundreds of parts per million of oil. Improvements in calibration and resistance to fouling were clearly needed. A design that keeps precision optics out of the water was developed. Figure 12 shows an arrangement with a diffuse reflector under water and all other optics above the surface. The cone shape of the reflector enables it to shed sediment through the hole at the bottom. The argon and neon lamps used in earlier designs have been replaced with germicidal, fluorescent black-light, and incandescent lamps, emitting at 254, 360, and about 600 nanometer wavelengths. Although the device is capable of detecting a wide variety of organics, only its

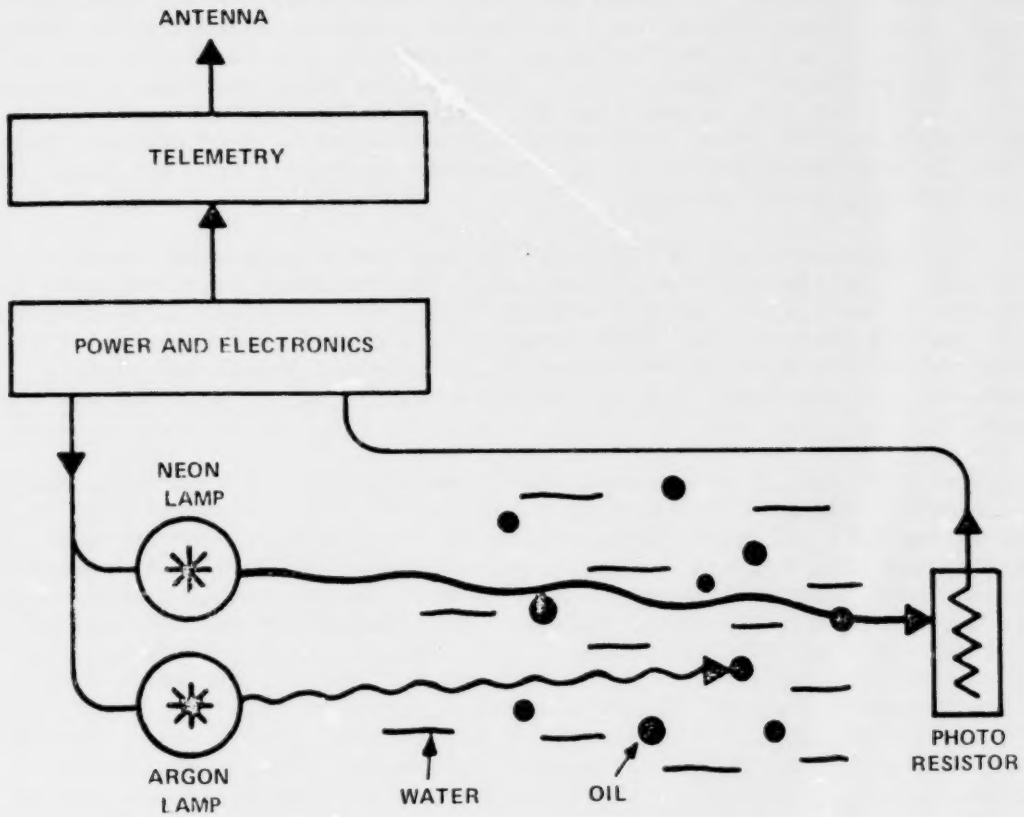


Figure 11 NEAR-ULTRAVIOLET OIL SENSOR

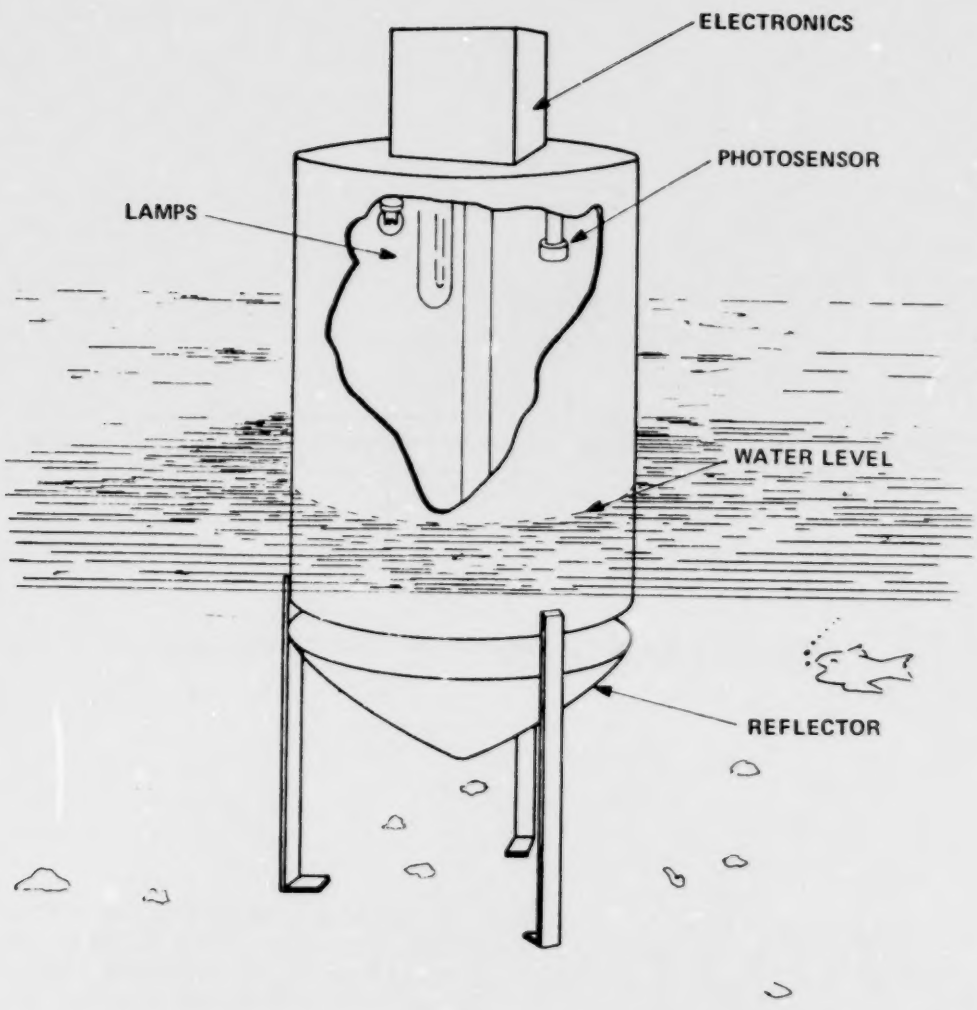


Figure 12 MULTISPECTRAL TRANSMISSOMETER

sensitivity to various oils has been demonstrated to date.

CYCLIC COLORIMETER

A major effort of the task on detection and monitoring centered on the development of the "cyclic colorimeter"* (Figure 13), an instrument designed

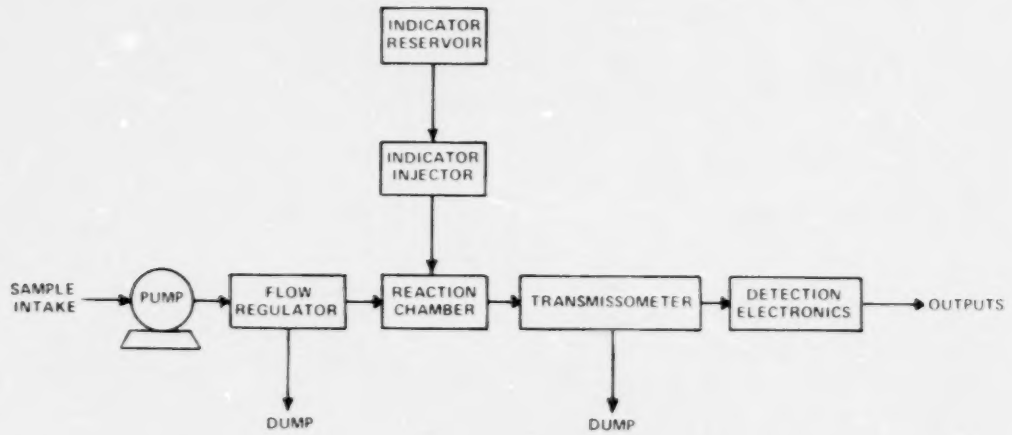


Figure 13 CYCLIC COLORIMETER – BLOCK DIAGRAM

for automatic detection of pollutants. (7) In this instrument, an indicator (for example, sodium sulfide) is injected periodically into a flowing sample of the water to be analyzed. Downstream of the point of injection, variations in the optical transmittance of the water are observed by means of a light source and photodetector. When the pollutant is present, cyclic variations in the optical transmittance of the sample stream occur at the indicator injection frequency, and are detected by the electronic subsystem. The electronics can be configured to yield either a quantitative indication of the pollutant or a simple alarm when a threshold pollutant level is exceeded. The various subsystems of the colorimeter are discussed in the following paragraphs.

* U. S. Patent 3,992,109.

Three different schemes for indicator injection were considered. In the original concept of the colorimeter, a pulsatile pump was envisioned as the indicator injector. Further consideration of the system led to the conclusion that the same effect could be obtained with much less power consumption, greater system simplicity, and improved reliability by replacing the pump with a soleroid valve moduating the flow from a pressurized or gravity feed indicator reservoir (Figure 14B). Laboratory experiments showed that any indicator remaining between the valve seat and the outlet to the sample transport tube at the end of the injection cycle leached into the sample stream very slowly, lessening the contrast in the sample stream and degrading the instrument detection limits. To avoid the leaching problem, a configuration (Figure 14C) in which the drops of the indicator solution fall through an air space within the reaction chamber to reach the sample stream was selected. This delivery scheme has the added advantage of a complete lack of moving parts in the injection system, with a resultant further improvement in reliability and power consumption.

Reaction Chamber

In the first prototype of the reaction chamber for the free falling droplet injector scheme, the chamber arm containing the indicator dropper was sealed to trap an air bubble in the arm. With this configuration, small air bubbles in the sample stream tended to accumulate in this arm, augmenting the trapped air bubble. The trapped bubble would grow until the pressure drop across it overcame surface tension, then a large section would break off and be carried downstream with the sample flow. This bubble would cause erratic readings from the transmissometer as it passed through. To eliminate this problem, the sample injection arm was vented to the atmosphere and the sample input and output lines were valved. With the valves properly adjusted, the Bernoulli effect just cancels the sample stream head, and a free surface at atmospheric pressure can be maintained within the injection arm of the mixing chamber.

A prototype of the reaction chamber was constructed from a standard, circular cross section, glass tee, but it was discovered that appreciable light was conducted from the light source to the detector of the transmissometer through the glass wall of the tee without passing through the sample stream. This stray light, of course, reduced the sensitivity of the instrument. To avoid the stray light problem, a second chamber with 3/8-inch square cross section was constructed from plexiglass. Although this chamber had dimensions similar to those of the circular cross section chamber, it was discovered that the opacity of the sample stream continued to increase for several centimeters beyond the output of the reaction chamber. (For proper operation of the colorimeter, there must be sufficient turbulence within the chamber to ensure adequate mixing of the indicator and the sample stream but not so much turbulence that the cloud of reactants spreads appreciably parallel to the stream flow.) Visual inspection of the flow conditions within the reaction chamber showed that the mixing within the square cross section chamber was quite different from that observed in the earlier, circular cross section chamber. Only a small fraction of the reagents actually underwent reaction within the chamber and the major portion of the resultant precipitate flowed out of the chamber without intercepting

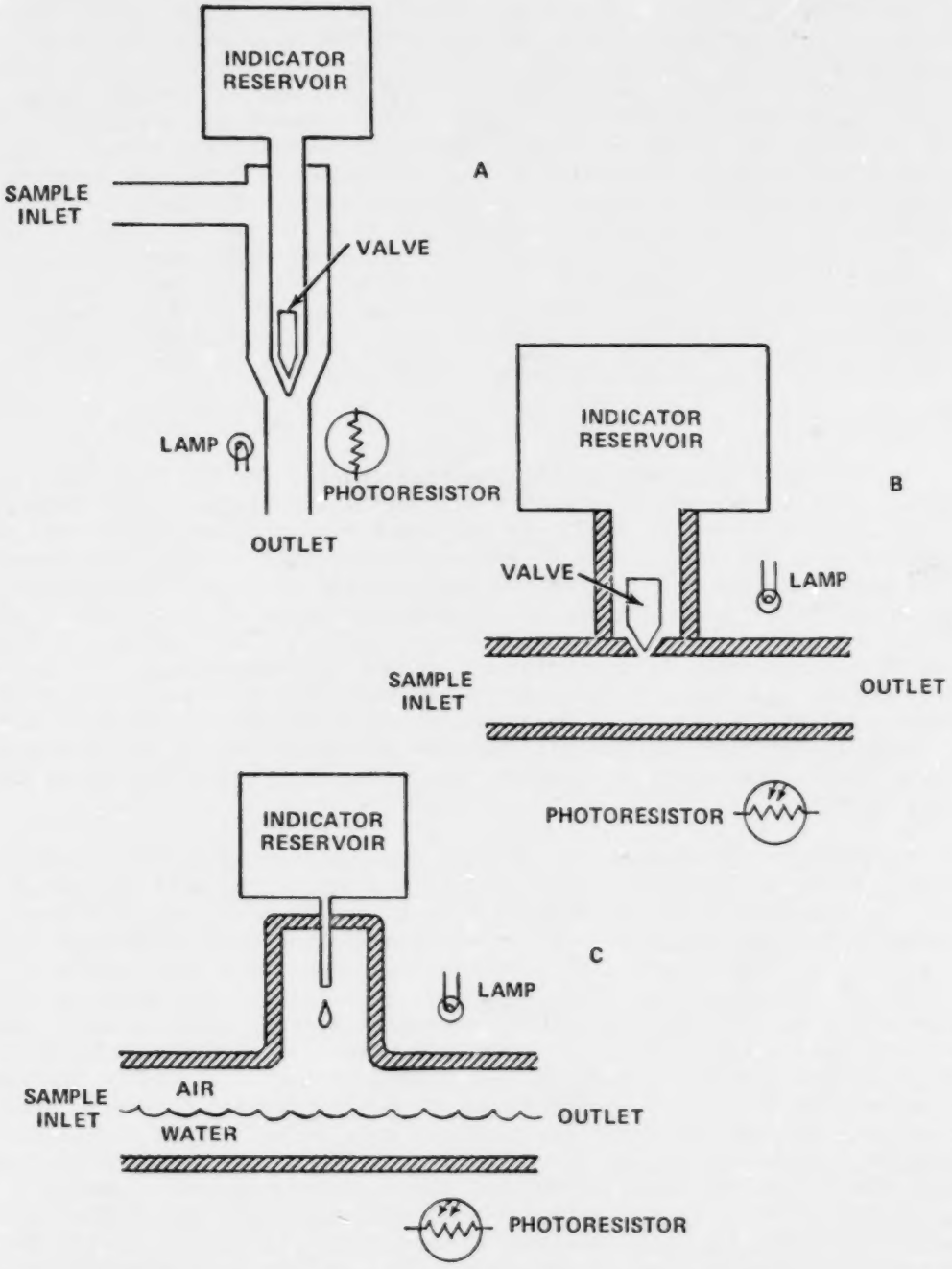


Figure 14 REACTION CHAMBER CONFIGURATIONS

the detector beam. When the flow rate was decreased to improve the reaction efficiency, accumulations of the precipitate rapidly fouled the chamber.

To induce mixing of the sample stream and the indicator and to prevent the accumulation of the precipitate, the reaction chamber was rotated 90 degrees and used in the configuration shown in Figures 15 and 16. The combination of the sharp corner in the sample channel and the occlusion formed where the exit tube joins the reaction chamber induces severe turbulence which ensures that the sample stream and the indicator are well mixed within the chamber and that the precipitate does intercept the detector beam. The air bubble prevents back diffusion of the indicator and, thus, increases the target-background contrast. With this configuration, the modulation of the photocell output for a given concentration of pollutant is increased by about three orders of magnitude over that observed with the earlier configuration. The sample stream flow rate is 0.5 ml/s with this plumbing configuration.

Figure 16 also shows the other significant aspects of the plumbing for the fieldable cyclic colorimeter. The filtered input sample stream is delivered to a constant head reservoir. The outflow from the reservoir is regulated by a needle valve and fed to the reaction chamber. The reaction chamber is vented to the atmosphere to prevent accumulation of air in the chamber and its outflow is regulated by a valve identical to that regulating the reservoir outflow. Since the valves regulating the input and output from the reaction chamber are identical, input and output rates can be made to track with variations in temperature and viscosity by choosing the respective heads to be equal. Any slight mismatch between the valves causes the fluid level within the chamber to shift slightly, varying the head and the output flow to compensate for mismatch. With this configuration, the cyclic colorimeter remains operable as the input sample stream temperature is varied between 5 C and 45 C. In one test, terminated after 72 hours, the colorimeter operated unattended at an indicator drip rate which would consume 2.5 liters of indicator per week--a rate certainly compatible with field installation of the instrument. The plumbing system, therefore, although extremely simple, is effective and reliable.

After being modulated by the injection of an indicator, the transmissivity of the sample stream must be measured. In keeping with the desired multipollutant response of an automatic detector, an unfiltered light bulb and a photocell were used to determine transmissivity. With this system, absorption in any portion of the optical spectrum will cause an instrument response. With sodium sulfide as the indicator, for example, sulfide precipitates of any color can be detected. Of course, such a wide optical bandwidth system will also see any coloration or turbidity in the sample stream (mud, algae, etc.) and any deposits on the walls of the reaction chamber (rust). The first scheme to eliminate the sensitivity to interferents was to AC couple the electronics to the photocell with a bandpass tuned to the indicator injection frequency. For a strictly AC coupled detector, the output is proportional to the fraction of the time during which indicator is present in the sample stream, making a duty cycle of about 50% desirable. With a synchronous detection system on the other hand, the duty cycle can be reduced almost arbitrarily without reducing the output signal. Such a reduction in

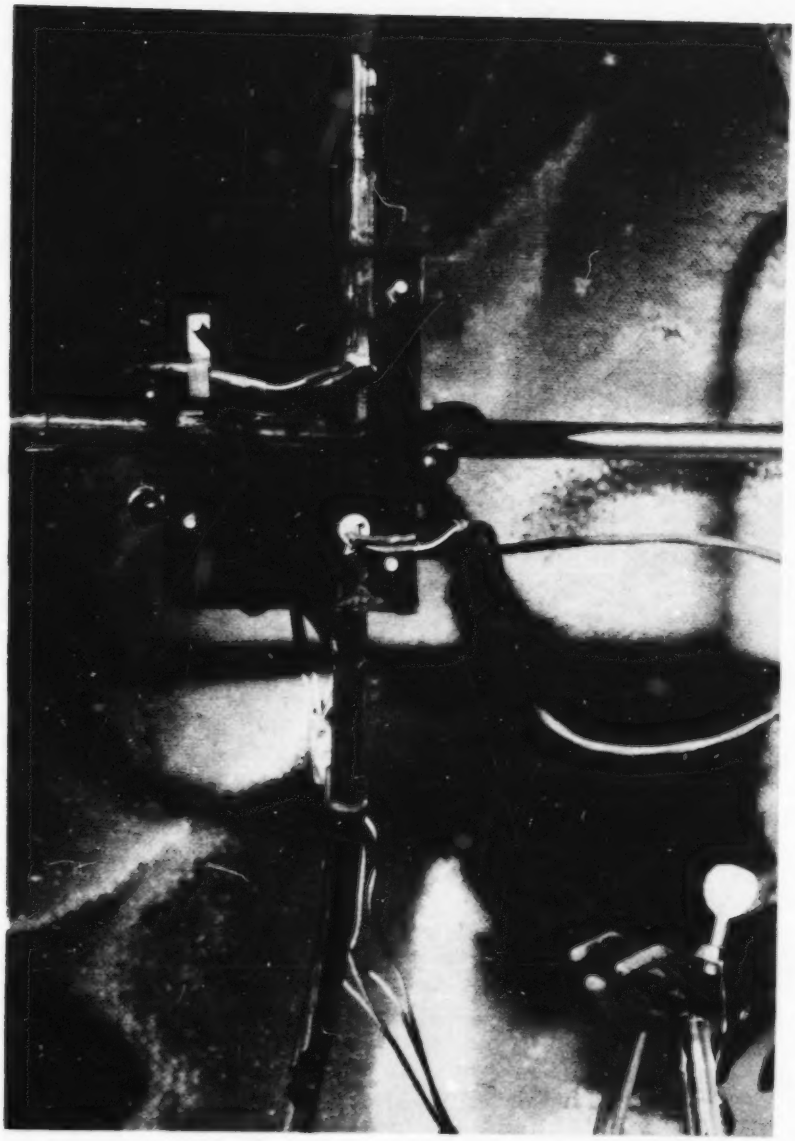


Figure 15 BREADBOARD OF CYCLIC COLORIMETER

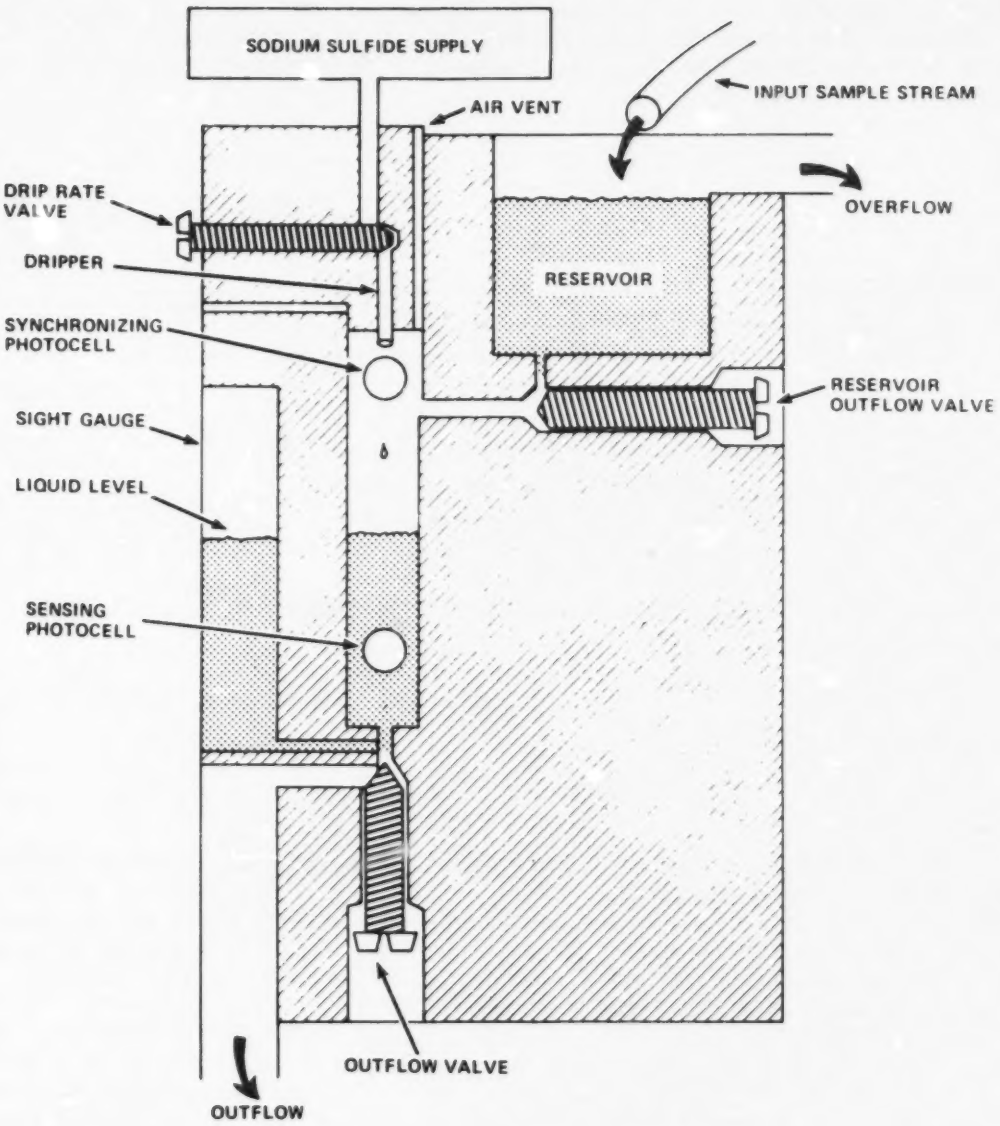


Figure 16 CYCLIC COLORIMETER PLUMBING

duty cycle saves considerable indicator solution and, thus, increases the field maintenance interval. Furthermore, with the freely dropping indicator injection system, injection frequency varies with temperature and time, very likely wandering outside the bandpass of the amplifier. A synchronous detector, however, can be cued to the falling of the indicator drop (sensed by another lamp-photocell combination) and maintain arbitrarily small bandwidth while tracking the injector frequency. The readout scheme selected is indicated in Figure 17.

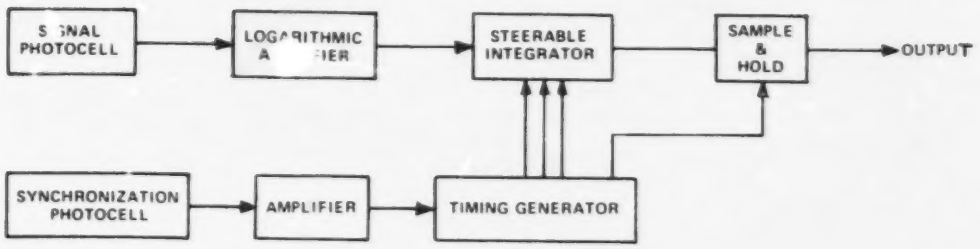


Figure 17 CYCLIC COLORIMETER ELECTRONICS – BLOCK DIAGRAM

The absorption signal from the photocell is applied to a logarithmic amplifier to expand the dynamic range of the instrument. The output of the logarithmic amplifier feeds a steerable integrator (8) which accumulates the absorption during the presence of the indicator with one sign and then subtracts from that signal an equal time integration of the sample stream absorption without indicator. The integrator is synchronized with the indicator drop by a lamp-photocell detector and suitable electronics. At the end of the integration cycle, the integrator output is accepted by a sample-and-hold circuit and becomes the output of the colorimeter. Note that this output is the difference between the logarithms of the sample stream absorptions with and without indicator, the logarithm of the ratio of these two absorptions. It is precisely this logarithm which is proportional to the concentration of the indicated substance by the Beer-Lambert law.

Electronics

The circuit diagram of the cyclic colorimeter electronics appears in Figure 18 and is discussed in detail in the following paragraphs.

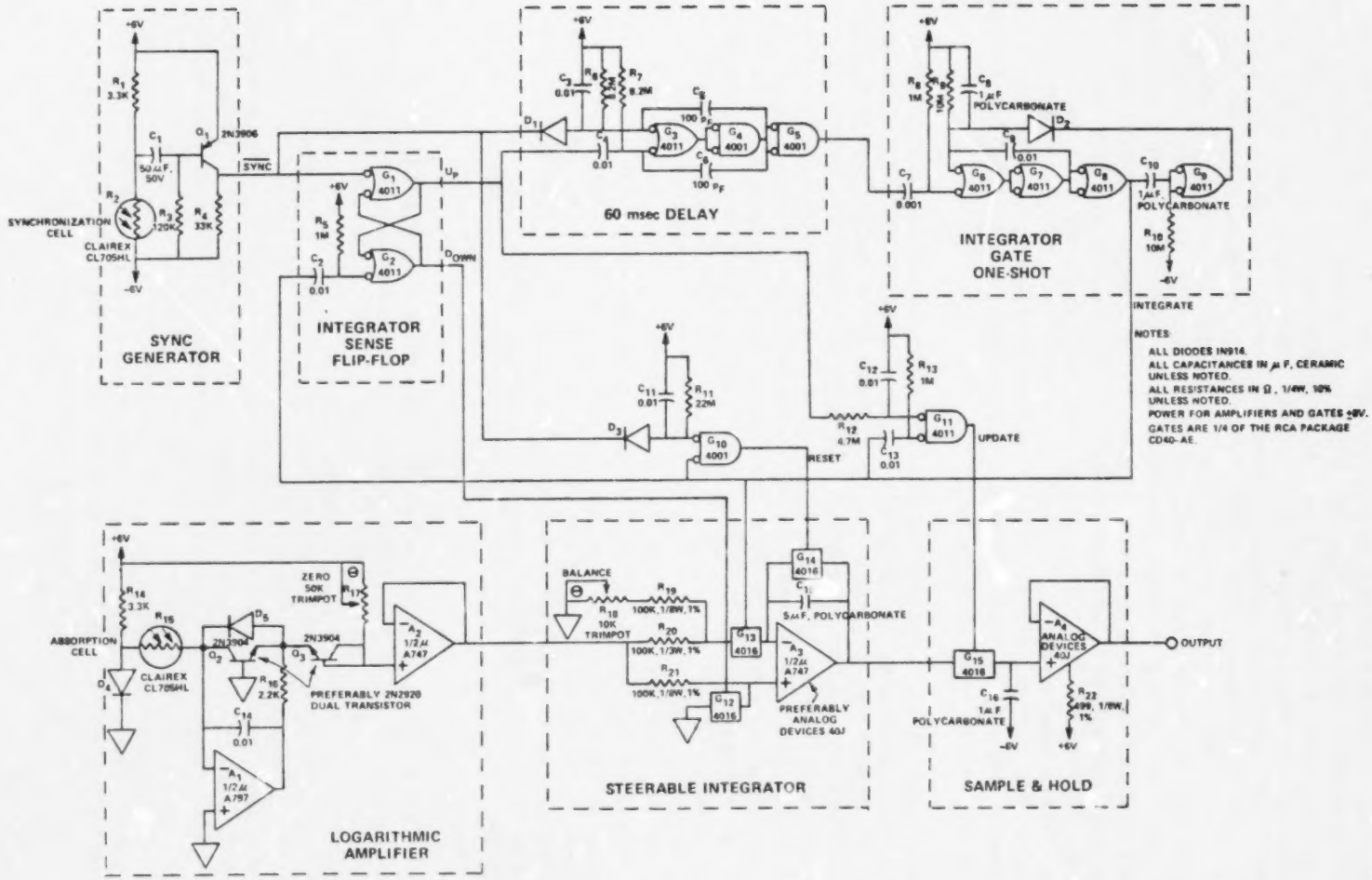


Figure 18 CYCLIC COLORIMETER ELECTRONICS – SCHEMATIC DIAGRAM

Consider first the analog portion of the circuit, the lower half of the schematic diagram. Resistor R_{14} and diode D_4 maintain a 0.7 V bias across the pollutant sensing photocell R_{15}. At constant voltage, the current from this photocell is nearly proportional to the input light intensity. Since the operational amplifier (ideally) draws no current and diode D_5 is ordinarily reverse biased, the entire input current becomes the collector current of Q_2. The voltage output from this stage is simply the emitter-base voltage of Q_2, which is proportional to the logarithm of its collector current (9). A bucking voltage developed by Q_3 (supplied with a constant collector current through R_{17}) compensates for the major temperature dependence of the emitter-base voltage of Q_2. In the breadboard colorimeter, Q_2 and Q_3 are individual 2N3904's. There were some problems with matching the two transistors adequately and a dual transistor such as the 2N2920 is recommended for future models. With clear water flowing through the colorimeter sample channel, R_{17} is adjusted to give zero output from the follower stage, which serves only as a buffer.

The output of the logarithmic amplifier drives an integrator whose direction of integration is controlled by analog gate G_{12} (8). With gates G_{12} and G_{13} closed and G_{14} open, input current flows only through R_{20} and is accumulated on C_{15}, as in a normal integrator. When G_{12} opens, however, both input terminals of A_3 follow the output from the logarithmic amplifier and the only input current that flows is through R_{18} and R_{19}. Since this current has the opposite sign from that which flows through R_{20} with G_{12} closed, the integration continues in the reverse direction. If integration proceeds in each direction for the same duration, the output from the integrator at the end of the cycle is proportional to the difference in the average values of the input over the time interval. This output should be sensed only with G_{12} closed to avoid picking up an offset due to the instantaneous value of the input voltage. G_{13} turns the integrator on and off and G_{14} resets it after an integration cycle has been completed. After the completion of the integration cycle and before reset, the output of the integrator is passed on to a conventional sample-and-hold circuit which provides an output approximately proportional to the concentration of the pollutant.

The appropriate array of pulses for the four analog gates is derived by the digital circuitry in the upper portion of Figure 21. The passage of an indicator drop between photocell R_2 and its illumination lamp causes a momentary increase in the resistance of the photocell. The resultant positive voltage pulse is AC coupled into the base of Q_1, turning this transistor off and allowing the voltage on its collector lead to drop. This negative pulse sets the integrator sense flip-flop, resets the analog integrator, and triggers the 60 ms monostable multivibrator. Capacitively-coupled positive feedback (10) is used to sharpen the fall of the multivibrator output pulse. This pulse triggers a 14 second monostable, which also has capacitively-coupled positive feedback to sharpen up its transitions. The output of the slower monostable turns on the integrator which, with G_{12} held open by G_2, integrates its input in the noninverting sense. The fall of the 14 s monostable, and integration resumes in the inverting sense. With the low output from G_1 satisfying one input of G_{11}, the fall of the 14 s

pulse triggers G_{11} and opens G_{15}, updating the output and completing the cycle.

Laboratory Tests

Calibration curves obtained with the cyclic colorimeter for the eight most common sulfide-treatable heavy metals and mercury are presented in Figures 19, 20, and 21. Detection limits are quite good for all the metals which form darkly colored sulfides. The poor detection limits for the lighter colored sulfides (ZnS -- white, MnS -- peach, and CdS -- yellow) could probably be improved by sensing light scattering rather than absorption.

A line of +1 slope has been included on each graph to indicate the theoretical dependence predicted by the Beer-Lambert law. The deviations of the actual data from this predicted behavior are not surprising considering the facts that the reactants are not very well mixed in the reaction chamber and that they are swept from the chamber in a time not very long compared to the reaction rates expected. It is interesting to note that despite the less than ideal chemical conditions, only in the case of the 0.1 M solution of Co^{++} is the carryover from one cycle to the next sufficient to cause a decrease in sample-to-background contrast with an increase in target element concentration.

The immunity of the cyclic colorimeter to background murkiness of the host stream was demonstrated using Fe^{++} ions as the target and powdered carbon as the interferent. Figure 22 shows recorder traces of the output of the colorimeter for slugs of 0.005 M Fe^{++} solutions in clear and dyed water. Note that, not only is the slug of pollutant easily detectable in the stream having a visibility of 1 cm, but also that there is no offset in the output baseline due to the carbon. Figure 23 presents calibration curves for Fe^{++} in clear water as well as in waters darkened with powdered carbon to give light transmissions of 50% and 5% centimeter (visibilities of about 4 cm and 1 cm, respectively).

These laboratory tests showed that the cyclic colorimeter had the potential of detecting multiple pollutants, even in extremely murky waters. To verify these laboratory results, a field evaluation was conducted.

Field Evaluation of the Cyclic Colorimeter

The laboratory tests outlined above were successful in detecting low levels of heavy metals in turbid water. The next logical step was to determine whether the concept could be implemented in the field. This effort was performed under a separate contract (No 68-03-0287) and consisted of four phases: Phase I, apparatus modification during which the laboratory prototype was made field-ready; Phase II, field installation during which the modified cyclic colorimeter was installed at a stream in the Buffalo, New York area; Phase III, field testing during which spills of a heavy metal simulant were made to determine whether the system could operate in an unattended mode for two weeks; and Phase IV, performance evaluation. Details of this work are presented below.

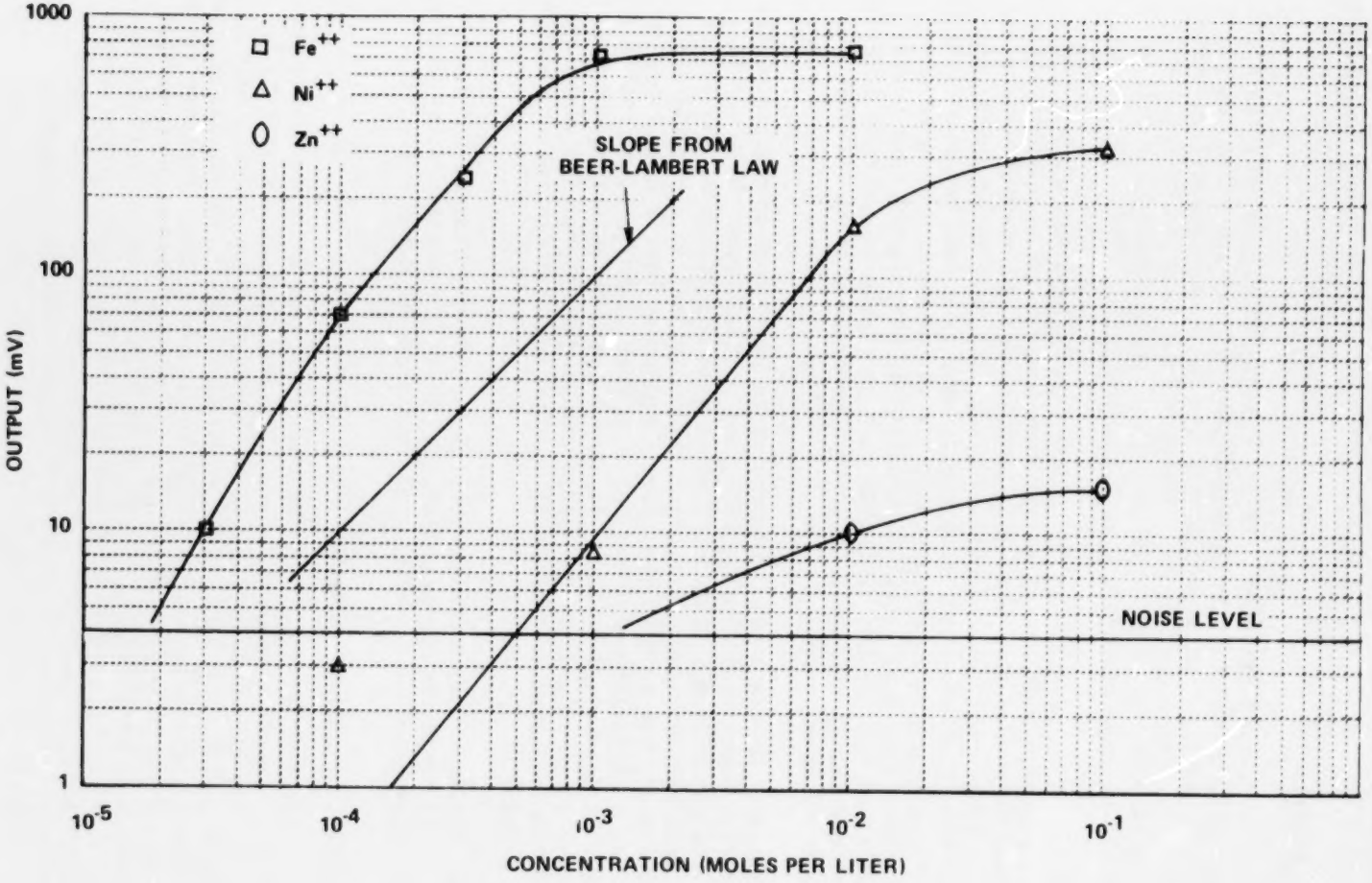


Figure 19 CYCLIC COLORIMETER CALIBRATION FOR IRON, NICKEL, AND ZINC

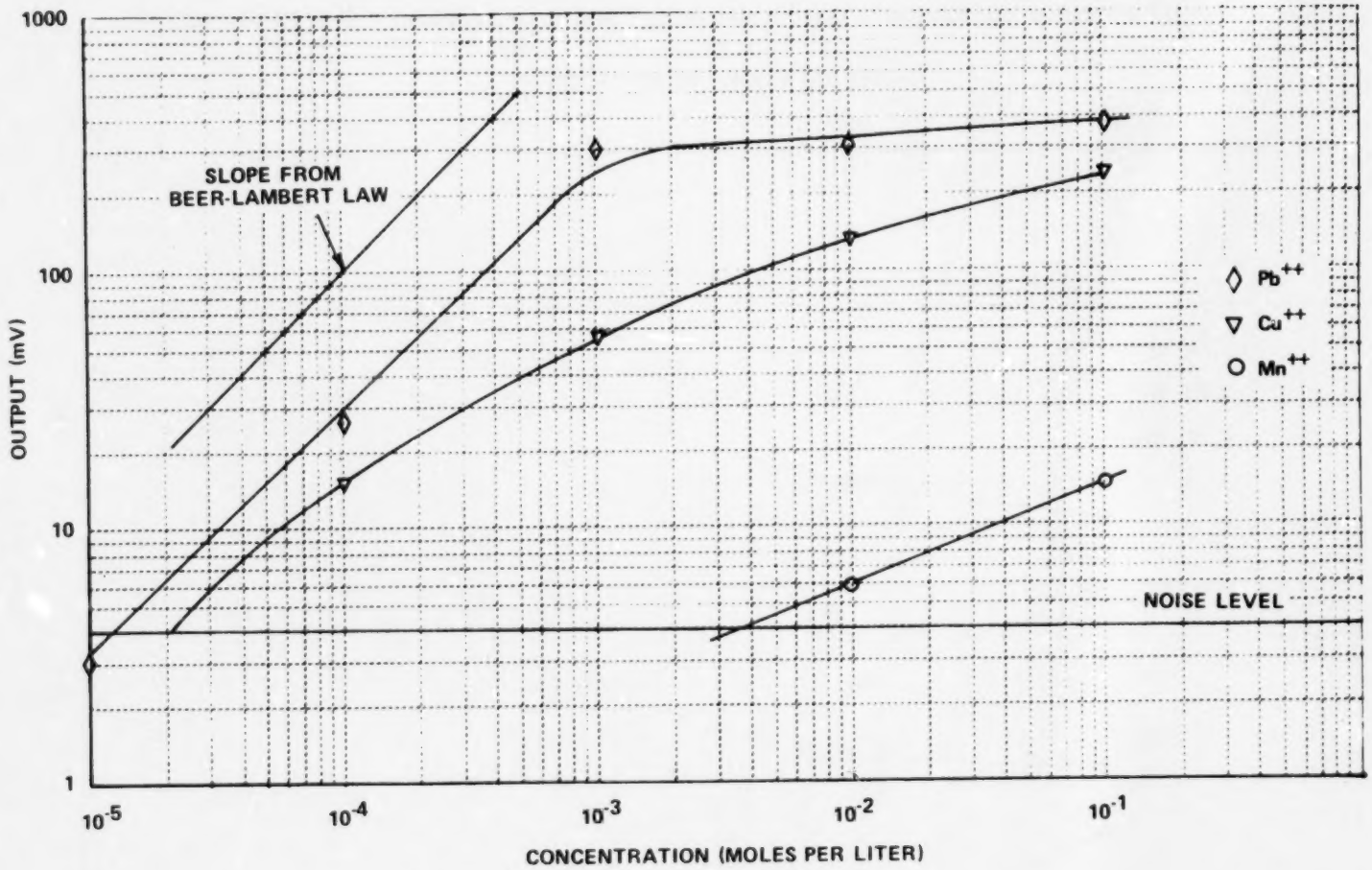


Figure 20 CYCLIC COLORIMETER CALIBRATION FOR LEAD, COPPER, AND MANGANESE

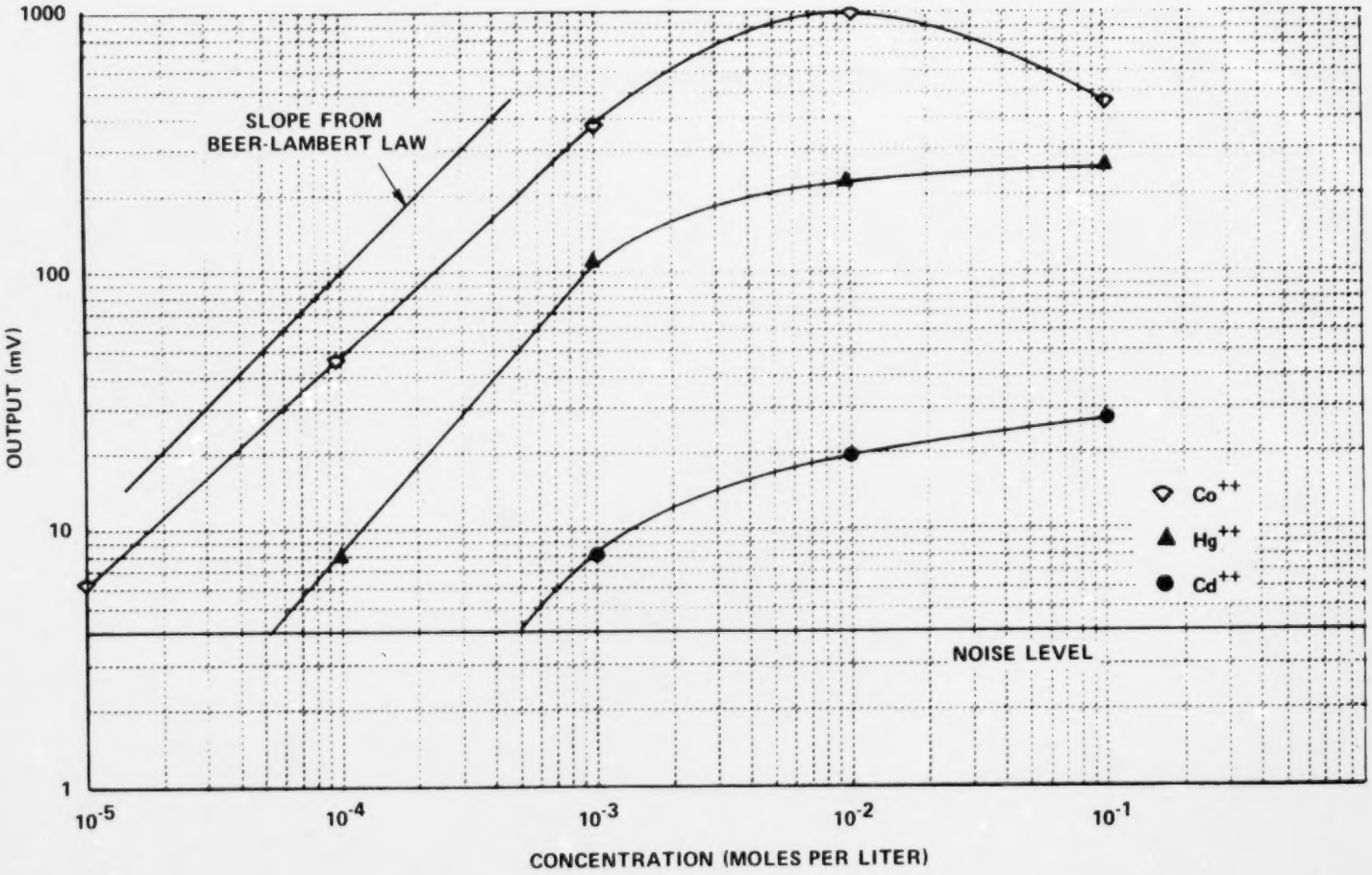


Figure 21 CYCLIC COLORIMETER CALIBRATION FOR COBALT, MERCURY, AND CADMIUM

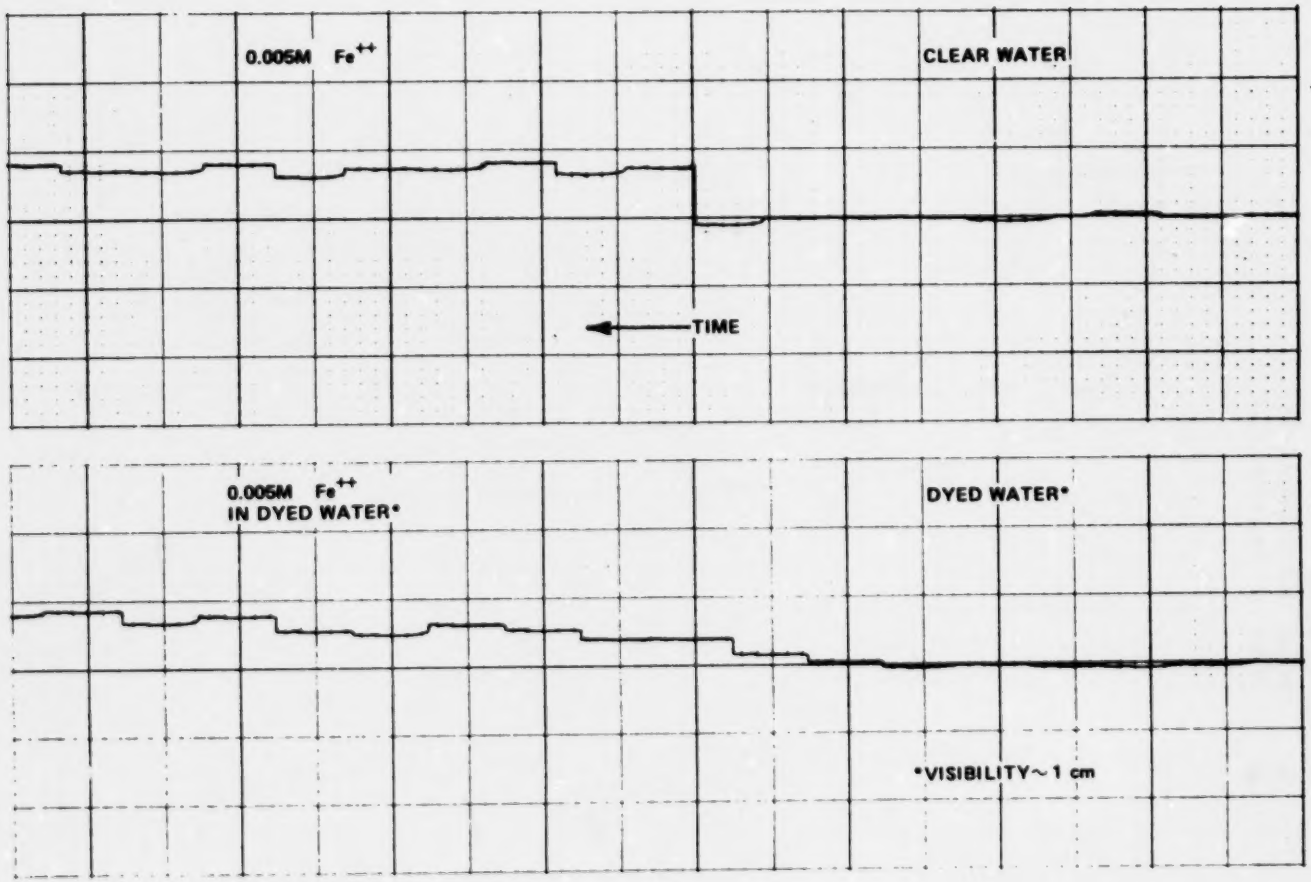


Figure 22 CYCLIC COLORIMETER RESPONSE

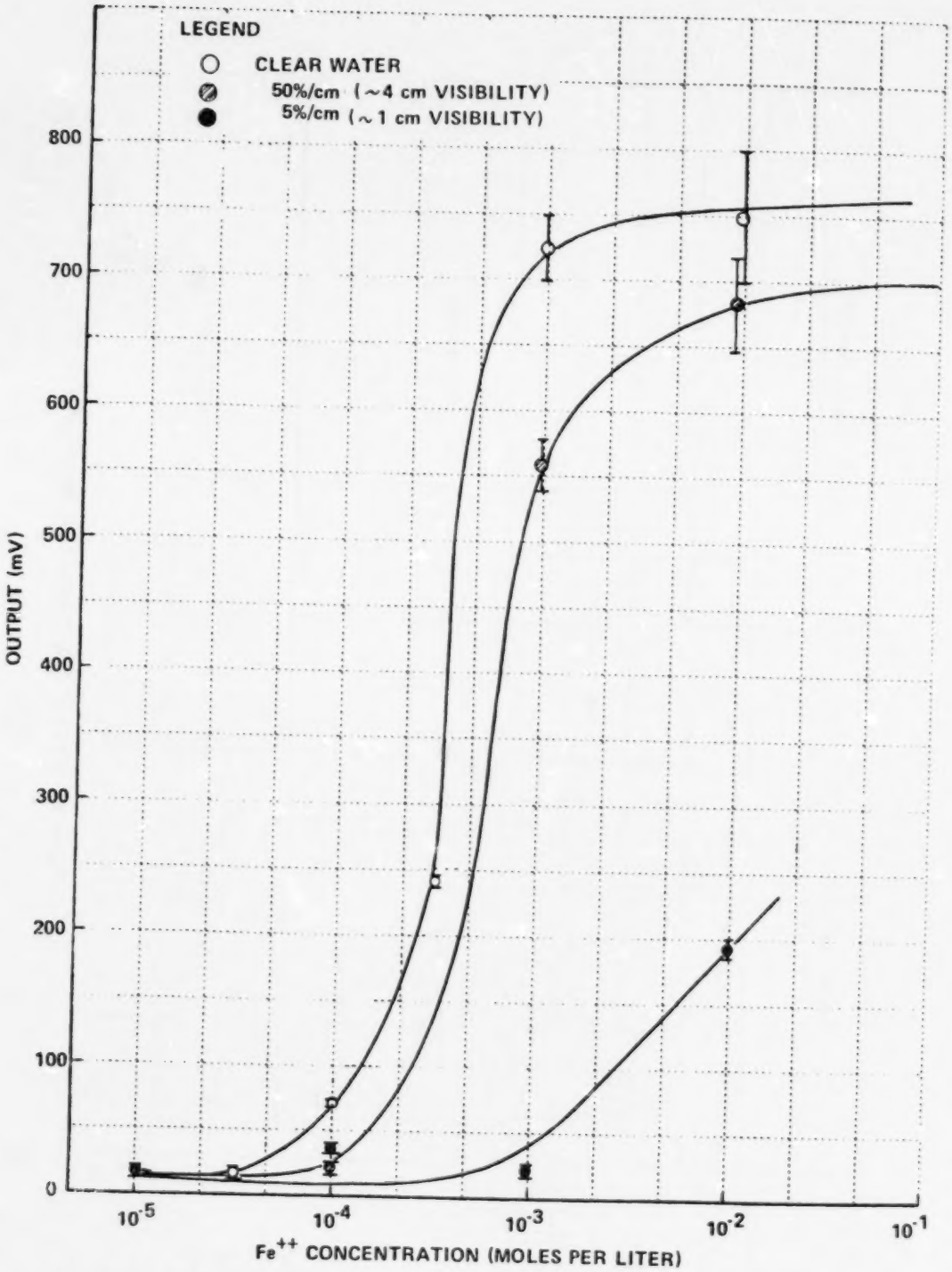


Figure 23 CYCLIC COLORIMETER CALIBRATION – TURBIDITY IMMUNITY

Apparatus Modifications--

The cyclic colorimeter comprises optical, electronic, and hydraulic components. Although satisfactory operation in a laboratory environment was demonstrated in 1971, improvements in electronic and hydraulic structure were needed for an instrument to be used in the field. The hydraulic structure that was originally contemplated used a sample stream to which indicator was added by a valve or pump at intervals sufficiently long to permit development of the color and flushing of the stream to restore the background condition. With this approach the large quantity of indicator that was used in a few days presented storage problems and might lead to incidental pollution. Indicator injection with a dropper mechanism permitted reduction of the size of hydraulic components but introduced new problems with drop rate control and regulation of the sample stream flow rate. These problems were overcome, and the hydraulic system that finally evolved is shown in Figure 24. It consists of a reaction chamber where optical transmission is measured by a lamp and photocell, two level control chambers, an orifice for stream flow regulation, and a distributed filter to control indicator flow rate. A second lamp-photocell combination senses the fall of the drop that initiates the measurement cycle. After the drop falls into the reaction chamber, transmission with indicator is measured for about twelve seconds, the time required to flush most of the reactants from the chamber. The background transmission without indicator is then measured during the interval from twelve to twenty-four seconds after the drop.

Sample stream flow is controlled by regulating the head, or pressure, above an orifice feeding the reaction chamber with a simple overflow chamber. The height of fluid in the reaction chamber is regulated by connecting it through a passage to another overflow chamber. All effluents are gathered in a single pipe that returns to the stream. In case a spill is detected all effluent could be stored for further analysis or reactants might be treated if a particularly toxic indicator were being used.

Field Installation--

The cyclic colorimeter was installed next to a creek about 45 kilometers south of Buffalo, New York, and received its input via a pipe that extended from the instrument installation to the central, most turbulent part of the creek (Figure 25). The pipe (A) about 3 cm in diameter, contained and protected a smaller tube (D) with an inside diameter of 6 mm which was connected to a foot valve (B) in the stream and a motor-driven pump (M, E) near the cyclic colorimeter. The pump was an automotive fuel pump especially treated for handling insecticides. The return flow is discharged into the 3 cm pipe and returned to the creek via a saddle tap and a piece of tygon tubing that trailed downstream and prevented recycling of samples.

Since the modified fuel pump consumed more power than all of the rest of the system, smaller pumps were tried but found to have insufficient suction head for operation at low water level. Power consumption was reduced, thus allowing battery operation during power failures, by cycling the pump to be on for three to four seconds every thirty seconds. With this duty cycle of ten percent, the pump flow rate of ten liters per minute was reduced to about one liter per minute. As a consequence of the cycling, considerable fluctuation in sample stream flow was expected and this led to the inclusion of an

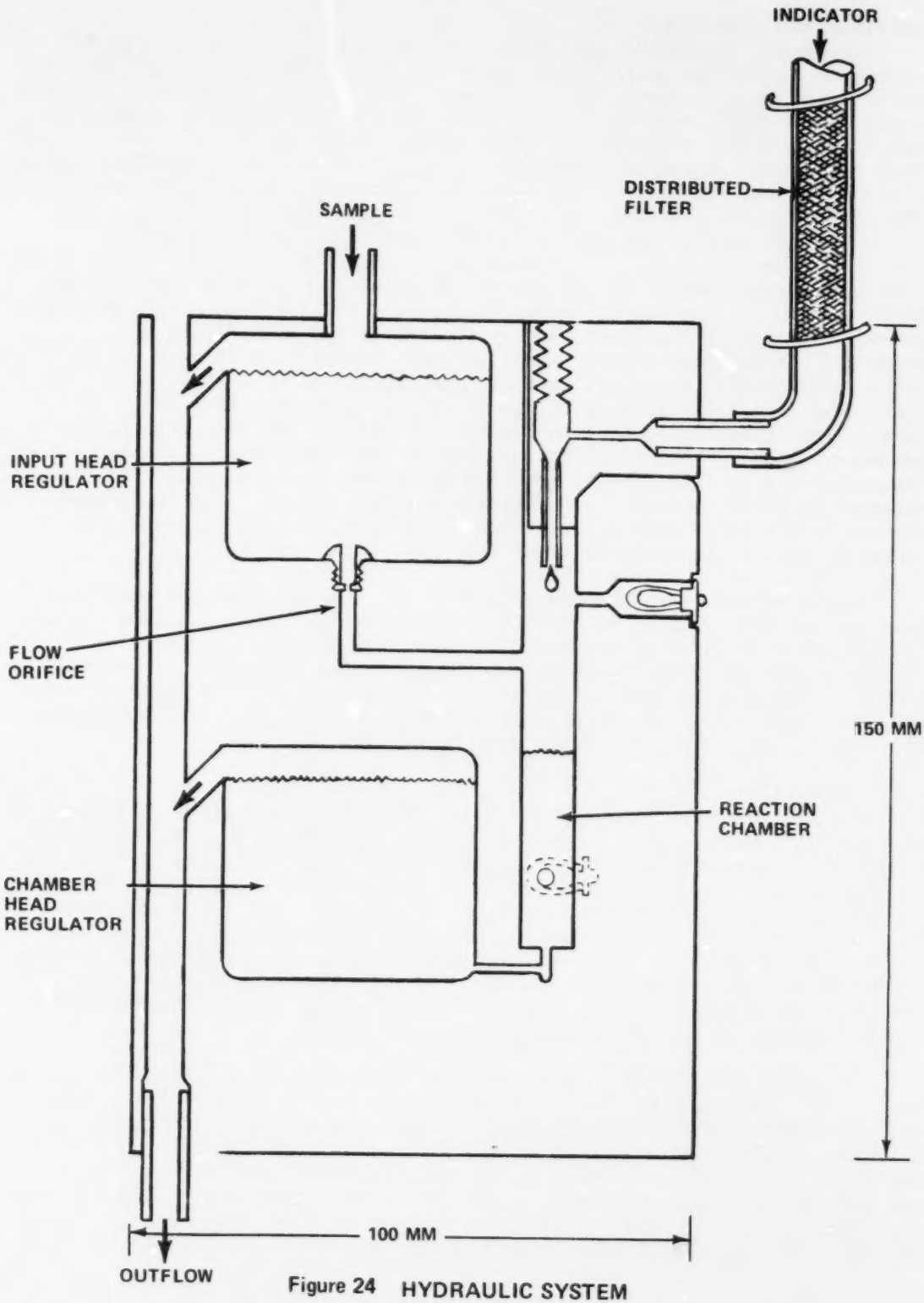


Figure 24 HYDRAULIC SYSTEM

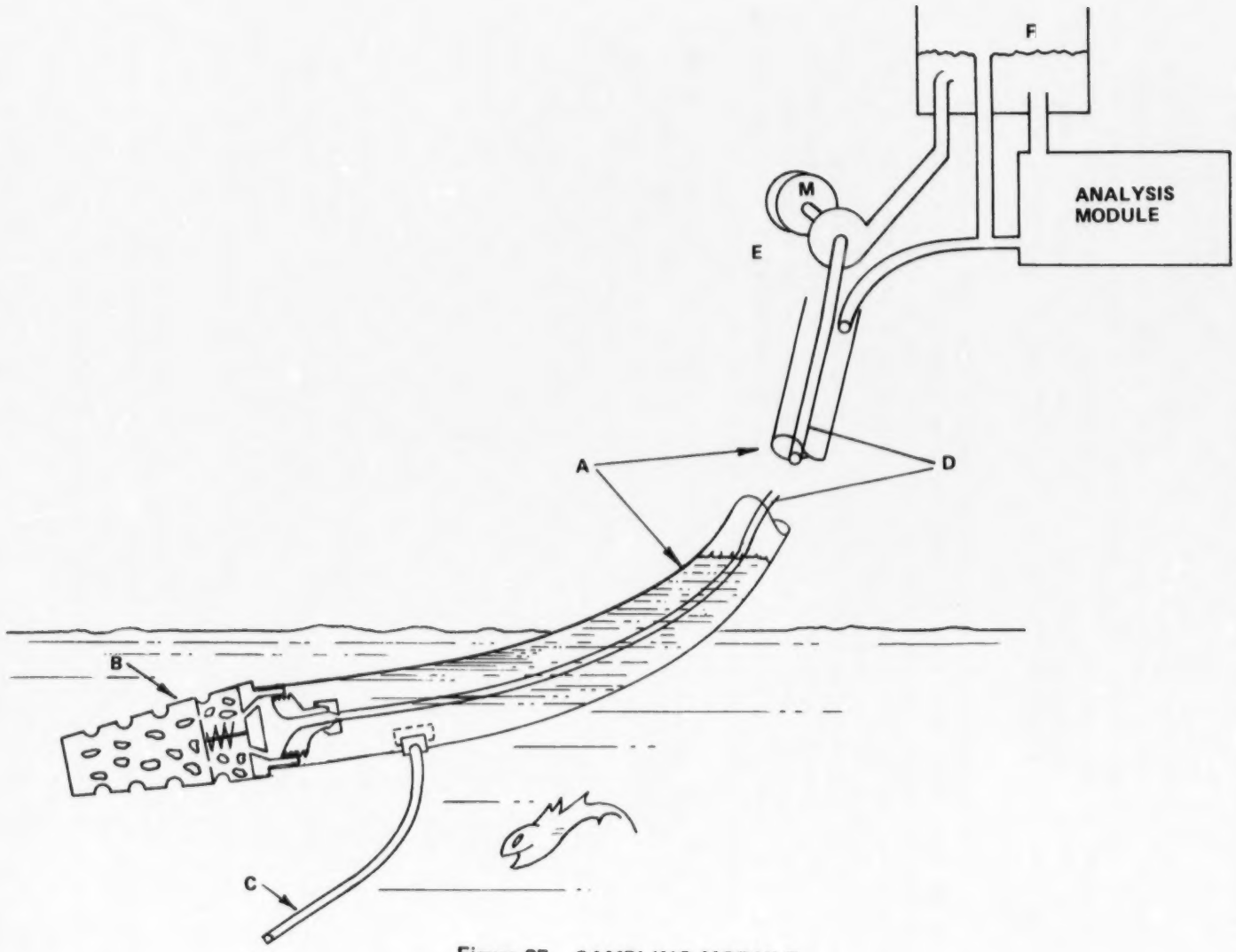


Figure 25 SAMPLING MODULE

additional intake level control chamber (Figure 26) that also acts as a settling basin for coarse sediment. The entire shore installation was installed in a utility cabinet (Figure 27). A pump, originally, in the lower left corner, fed the first level control chamber--an inverted plastic bottle--in the upper left corner whence the stream proceeded through the cyclic colorimeter in the center. Indicator was stored in a Florence flask in the upper right, while power supply and a recorder occupied the lower right of the cabinet. A 12 V storage battery was mounted in a separate case on shore. It was trickle charged and provided the surge of current for the pump as well as standby power for interruptions of line power of up to 48 hours.

Electronic components were mounted next to the cyclic colorimeter. The first of two 10x15 cm boards include the drop sensor, a logarithmic amplifier following the transmission photocell, and an integrator that was fed directly during the first 12 seconds following a drop and with an inverted input during the following 12 seconds. In this fashion the logarithm of the ratio of transmission with indicator to that without indicator is calculated. This number is related to the logarithm of pollutant concentration by the Beer-Lambert Law. It is stored for display on the recorder and updated 24 seconds after every drop. Timing is initiated by the drop sensor and performed in LSI counters by familiar techniques.

Additional amplifiers and electronic switches were mounted on a second board acting as an interface with a Rustrak recorder. This one-channel device was modified to record two channels, by sensing motion of the print bar with a mechanical switch that drove a binary divider or flip-flop. The flip-flop alternately connected either log transmission (density) signals or the stored pollutant concentration signal to the recorder meter movement. As a result, odd-numbered dots represent one signal and even-numbered ones the other, and since the dots of each moiety merge, two traces were generated. Further separation of the traces was provided by the use of the raw integral of the density signal which superposed a sawtooth modulation on it and left the pollutant record as a simple line.

Field Testing--

The apparatus was installed near the creek in August 1973, removed in January 1974 (Figure 28)--when the creek froze preventing acquisition of samples--reinstalled in May 1974, and removed in June 1974. Although some difficulties were encountered initially the device soon operated reliably, requiring maintenance only every two weeks. It was calibrated, by injection of a pollutant simulant, every week and blind tested several times by a simulated spill of ferrous sulfate.

Initially difficulties were experienced with the dropper control mechanism, a needle valve that swelled shut in the alkaline indicator solution. It was replaced with a distributed filter, generated by packing shredded fiberglass filter material between nylon cross hairs in a tygon tube. This type of filter, with no other obstacles in the indicator supply line, reliably produced a drop every forty to seventy seconds, could be trimmed slightly by squeezing and would last for about two months before enough glass fibers dissolved in the indicator to necessitate replacement.

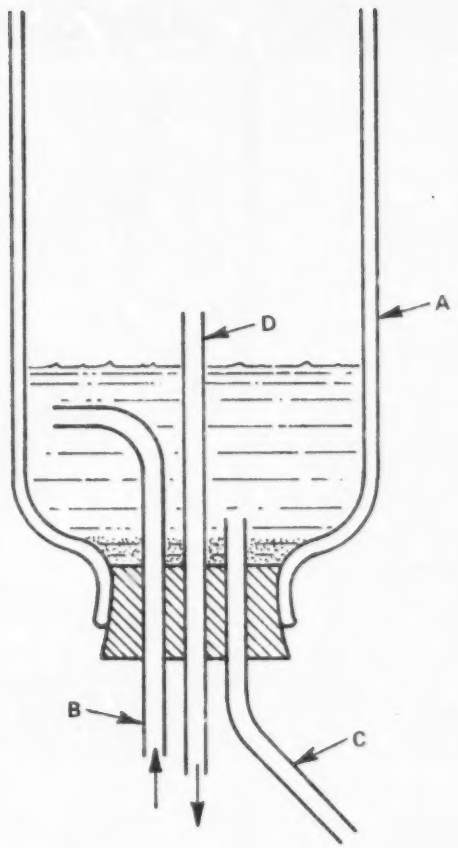


Figure 26 INTAKE LEVEL CONTROL

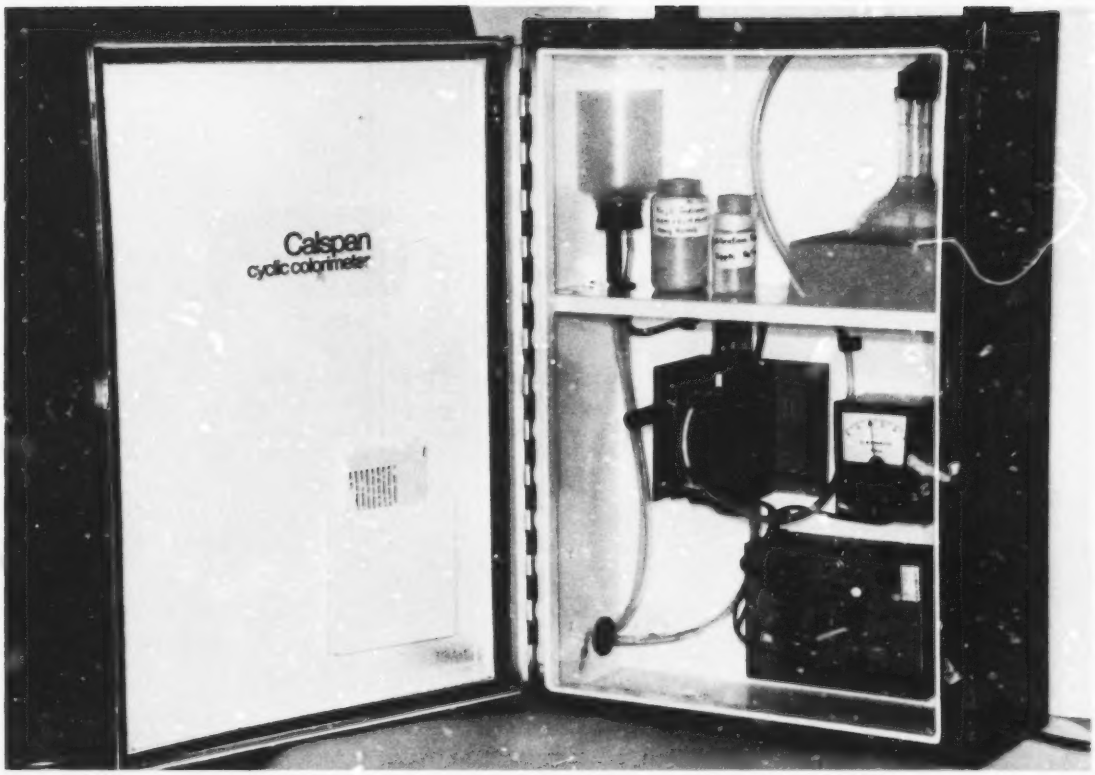


Figure 27 EXPERIMENTAL CYCLIC COLORIMETER

Figure 28 TEST SITE

In addition, an annoying problem arose with the drop detection sensor when it began to fail intermittently but only between 1 AM and 4 AM with the cabinet door closed. The problem was traced to AC ripple in the power supply that caused problems only when there was moisture condensation in the cabinet and the internal resistance of a Nicad battery was increased by temperatures below freezing. The electronic circuits were coated with hot paraffin to resist condensation, a ripple filter was installed, and this problem was eliminated.

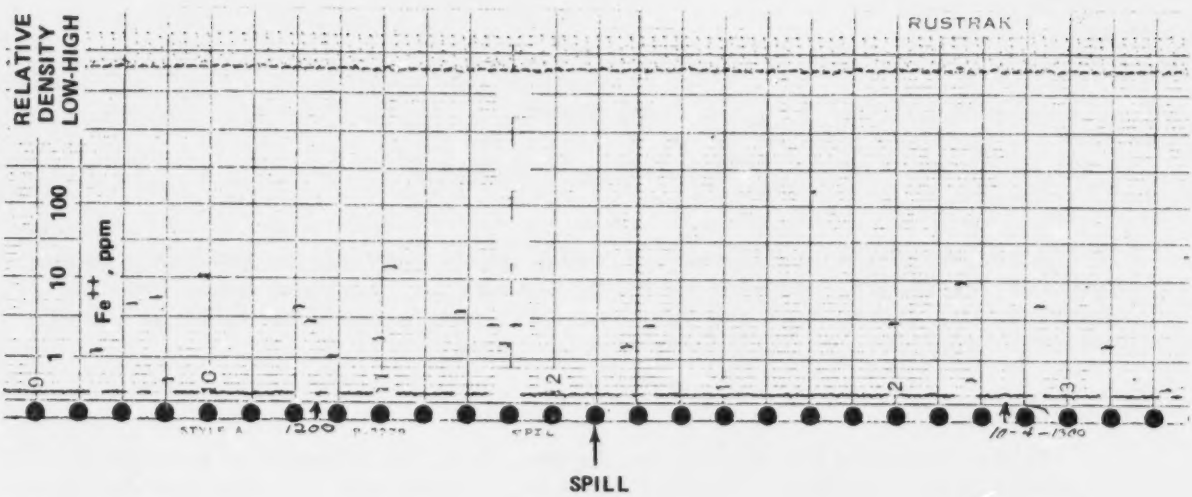
Throughout the evaluation, scale was found to deposit in the reaction chamber and effluent tubes by the reaction of calcium bicarbonate in the stream and OH ions in the indicator to form calcium carbonate. The scale would build up to the point where it interfered with measurements in about two weeks and had to be removed by flushing about 20 cc of concentrated hydrochloric acid through the colorimeter. In addition, paper was replaced in the recorder every week, the system was calibrated with known concentrations of ferrous sulfate solution and battery electrolyte levels and power voltages were checked.

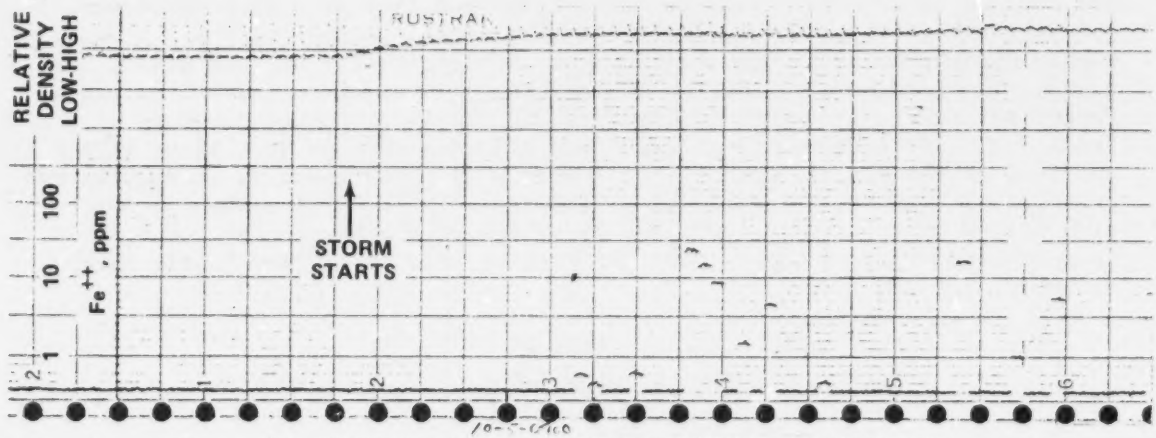
A few moles of ferrous sulfate in solution were injected into the creek about 25 meters above the sensor on several occasions. Detection of these spills on the recorder traces was in each case doubtful, primarily because concentration at the sensor was in the vicinity of one to three parts per million, that is, in the noise level. A separate test of the dissipation of a simulant spill indicated that both turbulence and precipitation of ferric hydroxide decimated the spill too quickly and that one should have made much larger and potentially harmful spills. A typical spill record is shown in Figure 29 and compared with the noise produced by the growth and decay of runoff turbidity before and after a rainstorm.

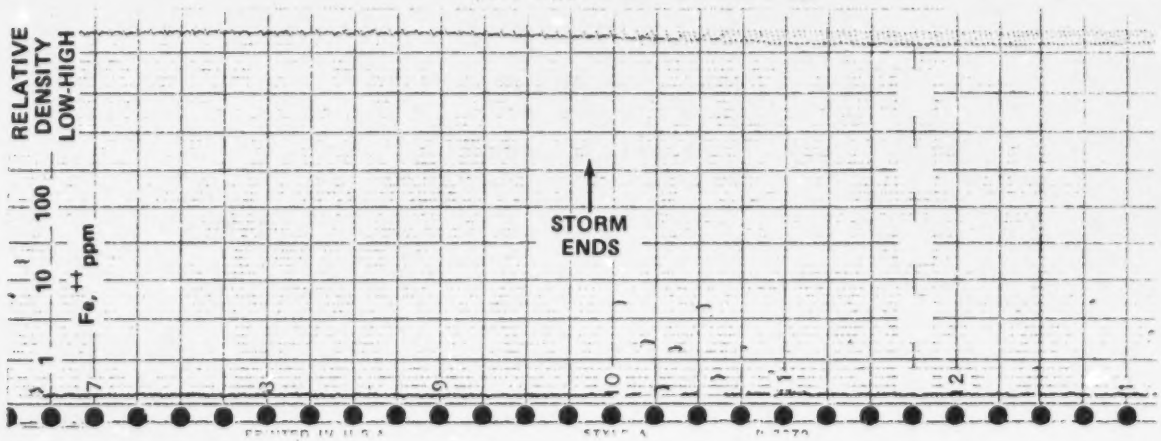
Performance Evaluation--

The cyclic colorimeter is a useful instrument for field monitoring of spills. An evaluation of its characteristics showed that it maintained adequate sensitivity of a few parts per million of heavy metal ion for a period of about two weeks without maintenance and despite noticeable fouling due to scale buildup and stream turbidity. It proved difficult to make a simulated spill that would not be suppressed by natural processes in the creek without spilling unconscionable quantities (tens of moles) of simulant. The cyclic colorimeter used in these tests was delivered to EPA at Edison, NJ, in 1975. A third generation version, modified slightly to facilitate production, is now available on the commercial market.

Figure 29 SPILL AND STORM RECORD







SECTION V

SPILL TRACING TECHNIQUES

A review of the history of hazardous spills compiled by EPA and a report on potential hazards compiled by Battelle Memorial Institute under EPA contract (6), showed that the many hazardous spills could be detected by pH, conductivity, odor, or sulfide or chromate precipitation.

pH

In developing a kit for use by laymen (e.g., volunteer firemen) to use in identifying spilled hazardous materials, a colorimetric indicator for pH was decided upon. Many citizens are already familiar with such pH measurement through their experience with swimming pools. Bromothymol Blue, the most common indicator, has a very narrow range of sensitivity and one with a more useful range was sought. Such a pH indicator, superior to several universal paper indicators in readability and reproducibility, was described by Yamada (11). It contains four indicators and goes through the colors of the spectrum in the pH range from 4 to 10 (Table 2). Furthermore, it remains red for pH less than 4 and violet for pH greater than 10. The change in color with one pH unit, with the possible exception of the change from pH 9 to 10, is sufficiently clear to override the masking effects of even fairly murky water.

Table 2

pH INDICATOR

5 mg	THYMOL BLUE
12.5 mg	METHYL RED
60 mg	BROMOTHYMOL BLUE
100 mg	PHENOLPHTHALEIN

(+100 ml H_2O, 100 ml EtOH
TITRATE TO GREEN WITH NaOH)

pH	COLOR
4	RED
5	ORANGE
6	YELLOW
7	GREEN
8	BLUE
9	INDIGO
10	VIOLET

ODOR

The potential of odor as a hazardous spill indicator was investigated by a team of Calspan psychologists. They concluded that smell tests are of little use if the spilled substance is already known by type and quantity, and are quite dangerous if the fumes are of toxic concentrations. The main purpose of a smell test kit would be to verify the identify, and perhaps concentration, of already-smelled odors. In the event that an odor is detected in the absence of any previous information that a spill has occurred, the observer may be alerted to a potential problem and initiate action as warranted. Odors as indicators may also be used to follow the geographic progress of spilled material in those cases where the dilution of the aqueous solutions produce fumes of nontoxic concentrations.

Tests were conducted to measure the sensitivity of the sense of smell in detecting several pollutants. Solutions in various concentrations, of chlorine, methanol, ammonia, acrylonitrile, and phenol were used to fill small, covered jars to approximately three-fourths capacity. These jars were given a coded designation on the lid. For each chemical, three or four measured concentrations were arbitrarily selected for testing, as well as several jars containing distilled water to serve as controls. A jar was shaken briefly and then uncapped for presentation to the subject. The subject rated the intensity of the odor as none, faint, moderate, or strong (recorded as 0, 1, 2, or 3, respectively). Random orders of presentation were used for each subject. Six subjects were presented with phenol (50,100, 300, 1000 ppm in water), acrylonitrile (100, 300, 1000, 4000 ppm), and four jars of distilled water. Six different subjects were presented with chlorine (20, 50, 100 ppm), ammonia (5, 10, 50, 100 ppm), methanol (4000, 10,000, 30,000 ppm), and three jars of distilled water.

The results indicated fairly reliable detection of the following concentrations:

phenol	100 ppm
acrylonitrile	1000 ppm
chlorine	20 ppm
ammonia	5 ppm

At lower concentrations of these chemicals and at all levels of methanol, the ratings tended to overlap with ratings given to water. The averaged results are shown in Table 3.

INDICATORS

The psychologists also undertook a study to define a simple method and set of colorimetric indicators with which a layman could make a preliminary identification of heavy metal pollutants. They found that sulfide precipitation could be used to identify a considerable variety of heavy metals and that precipitation of barium chromate, by using either barium chloride or potassium dischromate as an indicator, would serve to identify chromate and barium ions. These particular indicators also show what treatment should be used to alleviate the hazard. The ranges over which easily observable and

Table 3
SMELL INTENSITIES

AVERAGE RATING	CHEMICAL					
	AMMONIA	METHANOL	CHLORINE	PHENOL	ACRYLONITRILE	WATER
3.0		RELIABLE	X100			
2.5	X5		X50	X1000		
2.0	X50				X1000	
	X100		X20	X100	X4000	
1.5						X
		X30,000			X300	
1.0		X10,000			X100	X
	UNRELIABLE					XX
0.5						X
				X50		X
0		X4,000				X

CONCENTRATIONS ARE IN PARTS PER MILLION.

and readily describable differences in color and opacity allow the discrimination of the concentration of various heavy metals are indicated by the solid lines in Figure 30. The dotted lines indicate the extensions to the ranges possible under ideal circumstances. Below the stated concentration limits, the solution with indicator plus pollutant is indistinguishable from pure water containing the indicator alone, and above the upper limit the solution turns so opaque that no furhter changes with concentration are observable. This study also showed that benzidine dihydrochloride in 5% HCl could be used as a chlorine indicator with a clearly distinguishable response at 10 ppb concentration and a laboratory detection limit of 2 ppb.

SPILL TRACING KIT

A pollution detection kit (Figure 31) based on the above studies was assembled containing smell samples, a pH indicator, the heavy metals colorimetric indicators, and a conductivity meter of the type shown in Figure 6. A manual with instructions for using the kit was prepared. It was designed to require only a minimum knowledge of spill problems, chemistry, or engineering. A brief explanation of the principles involved in the use of each component of the kit is followed by instructions for using the component. Uses of the various tests are described in the sequence most likely to occur in the real world situation. A one-hour training presentation was found to be adequate for instructing a group of 21 volunteer firemen in Colden, New York, on detecting hazardous spills using: 1) the sense of smell; 2) the conductivity meter; 3) the pH indicators; and 4) the heavy metal indicators. Methods for estimating the rate of movement of spills were also covered in the training session.

Qualitative identification of actual substances is clearly difficult and should properly be left to a chemist. This does not say that treatment cannot be initiated with the limited information derived from the above kit. Frequently, one has an estimate of the quantity of material lost. For example, many times no more than a few pounds of a poisonous heavy metal compound are spilled. If the addition of a sulfide precipitation indicator shows such a compound to be present, one can safely apply a small amount of treatment. If one still discovers the metal ion downstream, one can continue with this approach until a chemist and a hydrologist can estimate the exact quantity of residual treatment needed. The treatment of an acid or base spill is even simpler. One can add enough neutralizing agent to bring pH into the range from six to eight. If one considers the complexity of first aid procedures mastered by fire and police department employees, it seems likely that fairly simple treatment procedures can be carried out as described above.

IN SITU COLORIMETRY

The possibility of using colorimetric indicators added directly to the polluted body of water to assess the extent of the pollutant and the progress of the treatment was also investigated. It was envisioned that a stripe of an appropriate indicator solution might be laid down across the suspected spill area from a low-flying aircraft, and the dimensions of the spill determined from the aircraft on a second pass at a higher altitude.

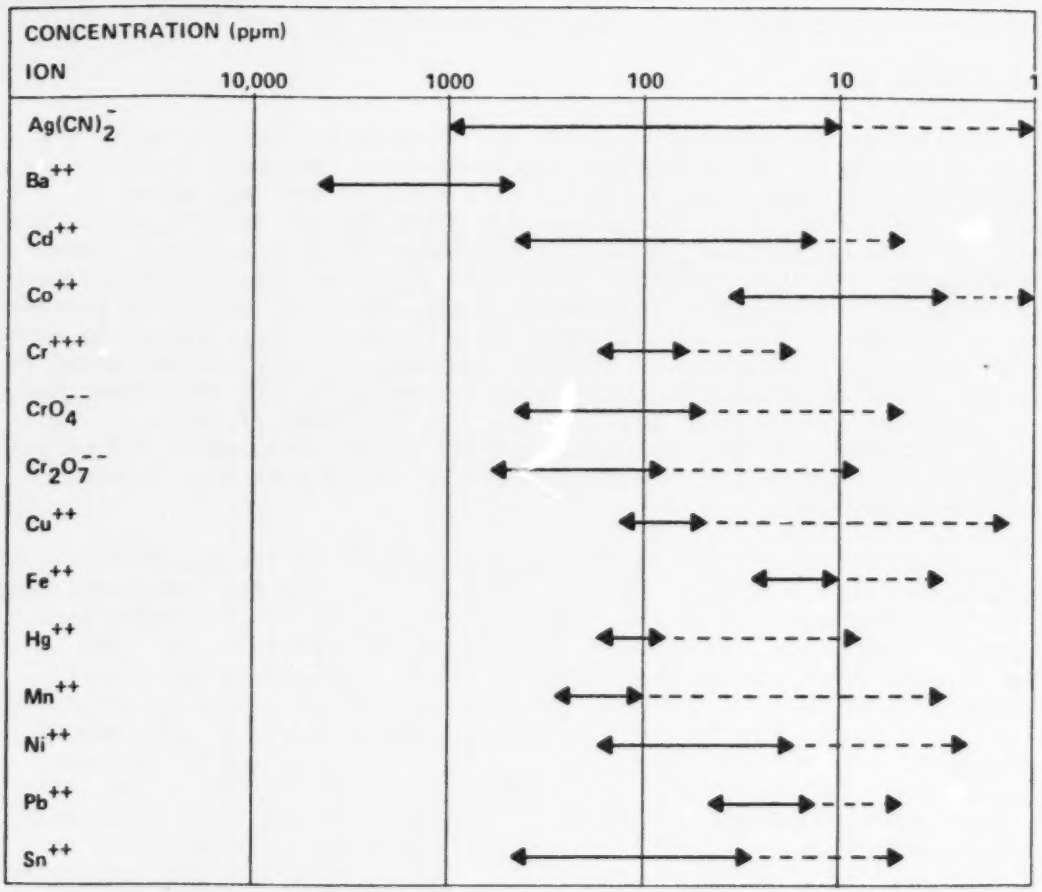


Figure 30 COLORIMETRIC DISCRIMINATION RANGE

Figure 31 SPILL TRACING KIT

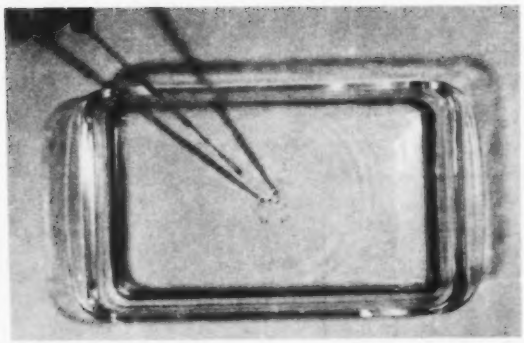
Laboratory experiments showed quite promising results (Figure 32). A field test with a pH indicator stripe applied from a boat across an industrial outfall of pH 4, however, failed to provide adequate contrast to permit the delineation of the outfall from the ambient pH 7 water. The dark background of the river bottom made reliable determination of the indicator color impossible.

DYE TRACER EXPERIMENTS

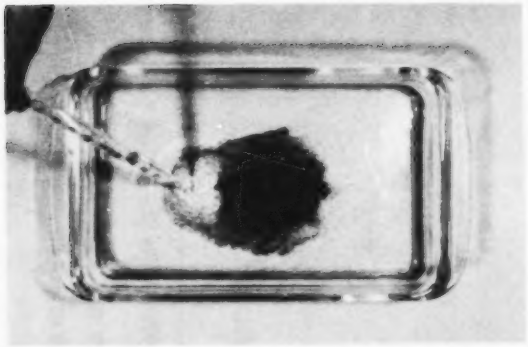
In some spill situations, one may be able to add an identifying dye to the spilled chemical before or shortly after it enters a waterway. The reactions of dyes which might be used to tag spills of certain heavy metal compounds were investigated. Table 4 displays the results of an experiment performed with the indicated chemicals and the dyes, rhodamine B and fluorescein sodium. One drop of dye was introduced into (1) a 50 ml, 0.1 M test sample of the chemical, and (2) a 50 ml test sample of water. The two samples were than compared under an ultraviolet light.

As indicated in the table, the majority of the heavy metal compounds exhibited only moderate suppression of the rhodamine B and flourescein sodium fluorescences or showed no apparent change. On the other hand, silver nitrate and cobalt chloride changed the color of fluorescein sodium and completely suppressed its fluorescence. On the basis of these observations, rhodamine B is usually preferred as a tracer because of less interference from the metallic ions involved in the spill.

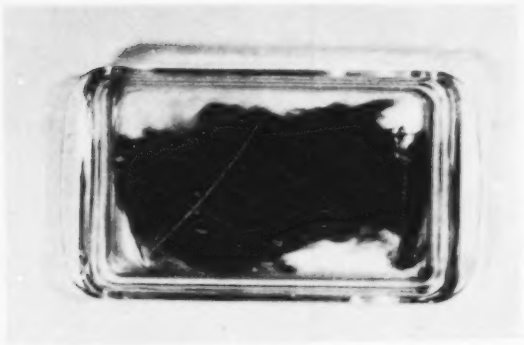
As little dye as possible should be used to minimize cost and harmful side effects of the dye, while assuring detection of the spill boundary at a significant pollutant concentration. Rhodamine B and fluorescein sodium can be detected visually at dilutions of about fifty parts per billion, and at lesser concentrations with fluorimeters. To apply one of these dyes to a chemical that should be detected at a level of one part per million, one pound of dye would be needed for every twenty pounds of pollutant. If several barrels of pollutant are spilled, the cost of the tracer is probably acceptable; if tank car quantities are spilled, it is not.



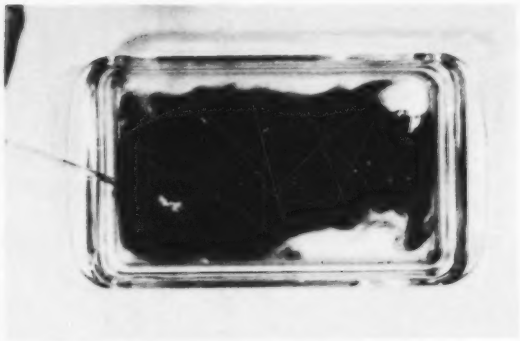
A. PERPETRATING THE SPILL



B. ADDING AN INDICATOR STRIPE

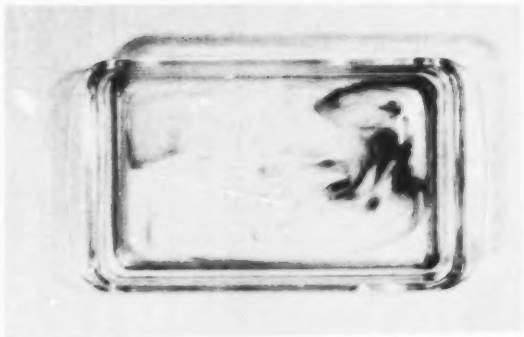


C. THE SPILL SPREADS



D. ADDING THE TREATMENT

E. SPILL PARTIALLY NEUTRALIZED



F. ALMOST TOTAL NEUTRALIZATION

Figure 32 COLORIMETRIC MONITORING OF TREATMENT EFFICACY – LABORATORY SIMULATION

Table 4

ATTENUATION OF DYE FLUORESCENCE BY SELECTED HEAVY METAL SALTS

SALT	DISODIUM FLUORESCEIN	RHODAMINE B
AMMONIUM MOLYBDATE	MODERATE	MODERATE
ZINC CHLORIDE	MODERATE	MODERATE
SILVER NITRATE	COMPLETE--ARMY DRAB GREEN COLORATION	NONE
SODIUM CHROMATE	MODERATE	MODERATE
SODIUM ARSENATE	NONE	NONE
CADMIUM CHLORIDE	MODERATE	NONE
MANGANOUS SULFATE	MODERATE	NONE
COBALT CHLORIDE	COMPLETE--BUFF COLORATION	MODERATE
NICKELOUS SULFATE	MODERATE	MODERATE
BARIUM ACETATE	NONE	SLIGHT

SECTION 6

SUMMARY

This investigation has shown that it is possible to detect a wide variety of spilled hazardous materials with simple, fieldable instruments. While the limits of detection are not always below the limits of toxicity, minor discrepancies are not critical for two reasons. First, the target of the automatic detectors is the acute spill. Quoted toxicity limits are usually based on prolonged exposure and are usually lower than the minimum concentrations damaging in acute exposure. Detection of chronic pollution near the toxicity level can be implemented by more sensitive laboratory determinations made periodically on a sampling basis. Second, the detectors are to be placed in likely spill locations where they will intercept the spill before it undergoes much dilution. Little of the environment will experience the pollutant at or near this concentration.

Simple and effective procedures to enable laymen to identify spilled hazardous materials have also been developed and demonstrated. Only minimal instruction in the performance of these procedures is required.

Finally, dyes suitable for tracing heavy metal spills have been suggested.

Improvements in detection limits, equipment reliability, maintenance intervals, and economy are certainly desirable in many instances, but a quite significant start has been made in providing the technology for a nationwide hazardous spill detection network.

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